JOURNAL OF

# CHEMICAL EDUCATION

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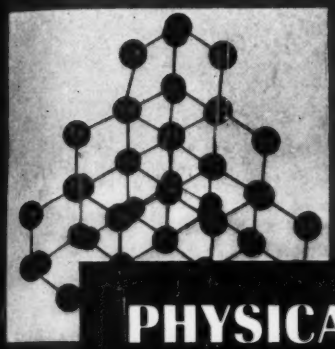

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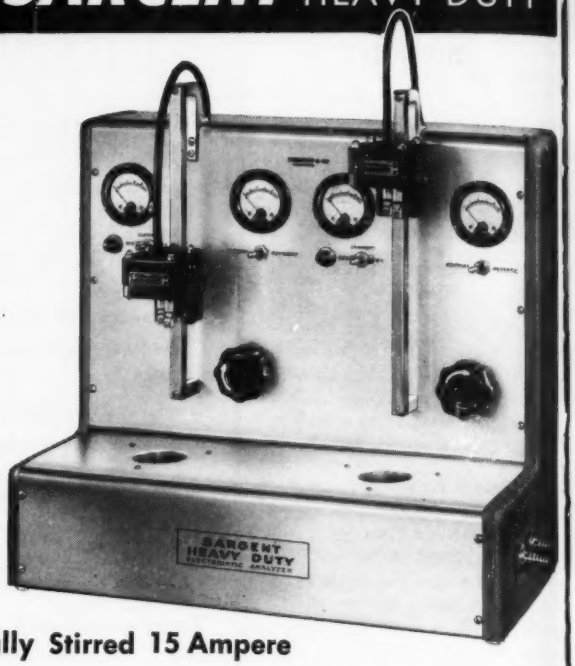


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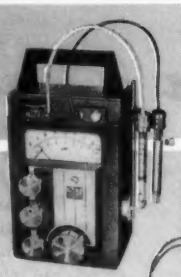

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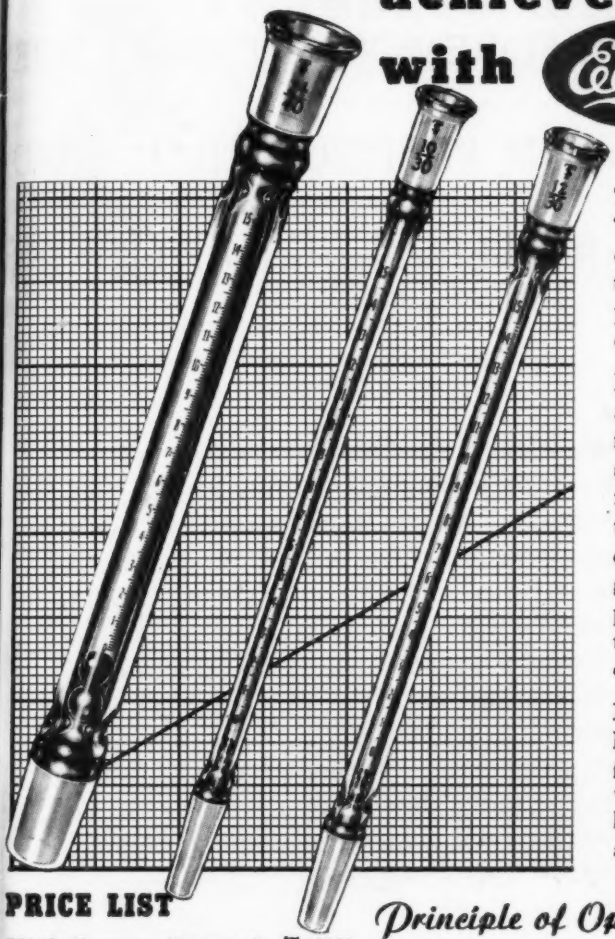

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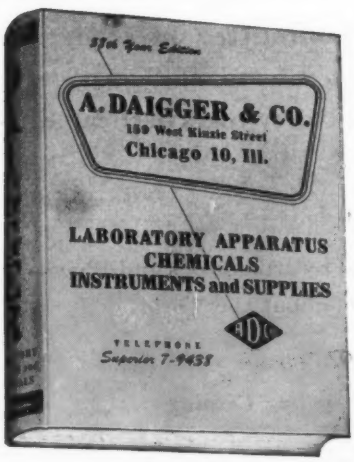


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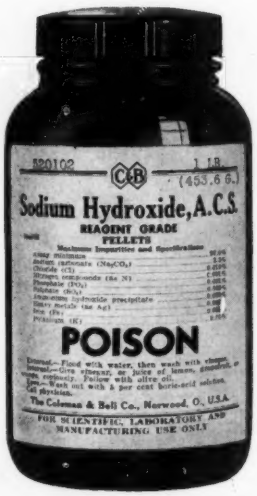


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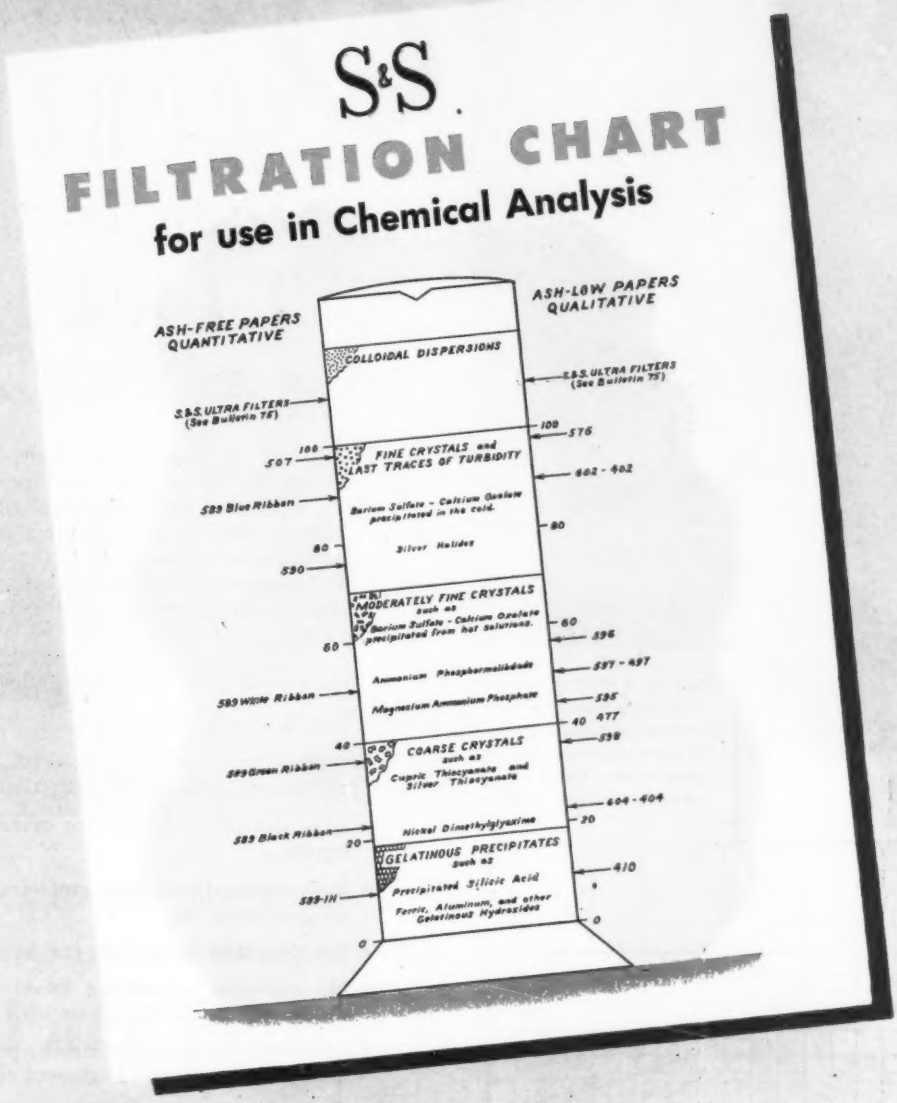


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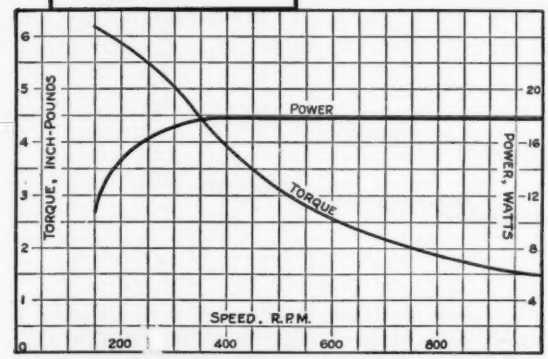


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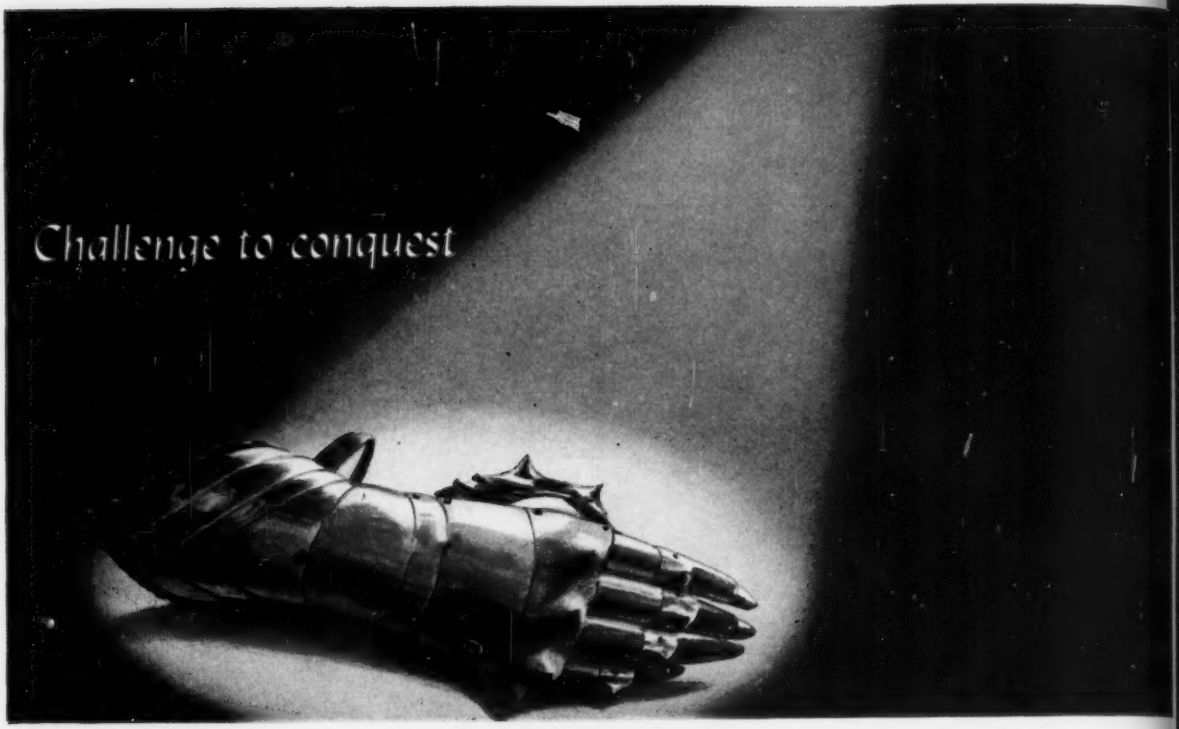


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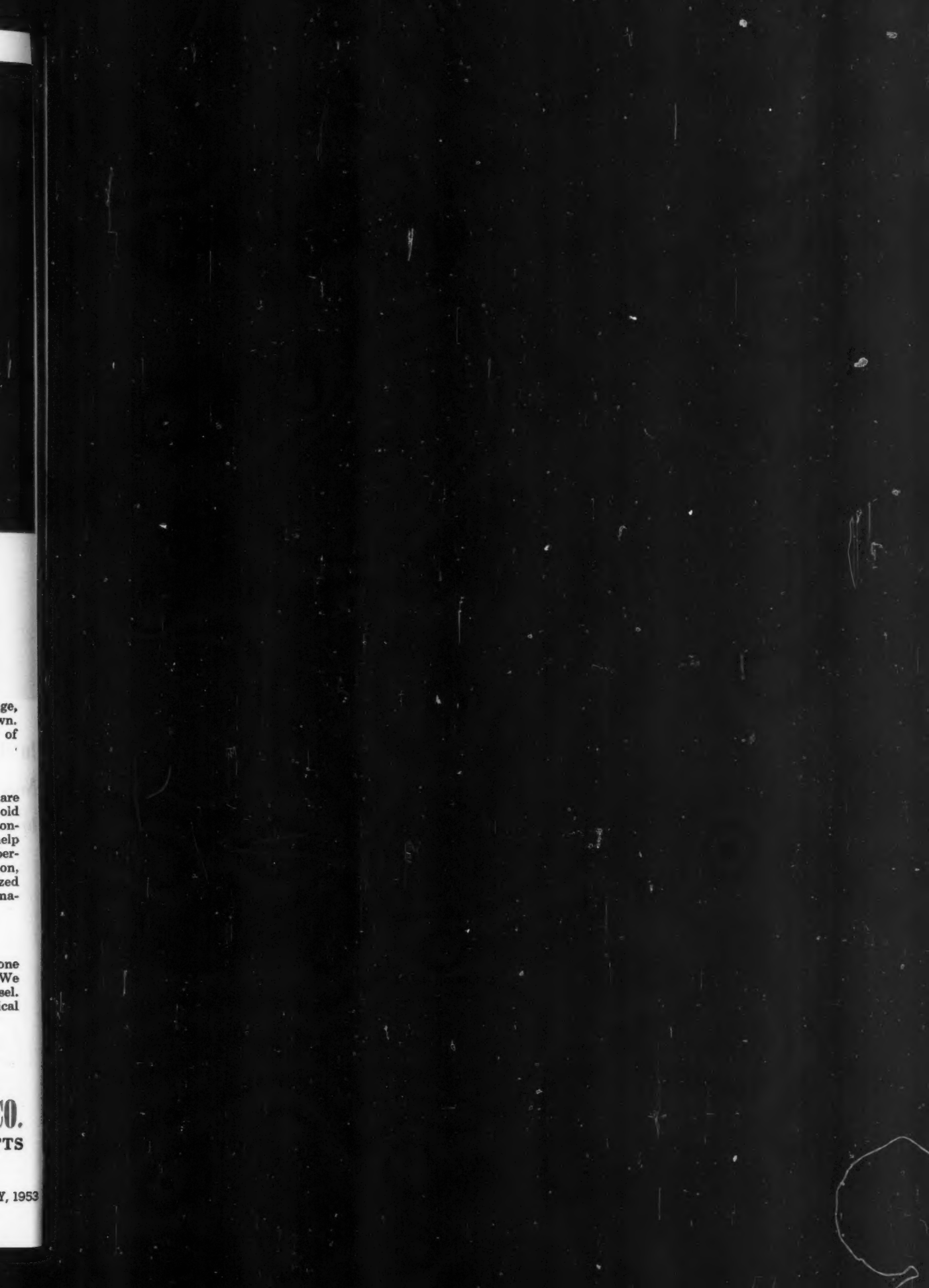

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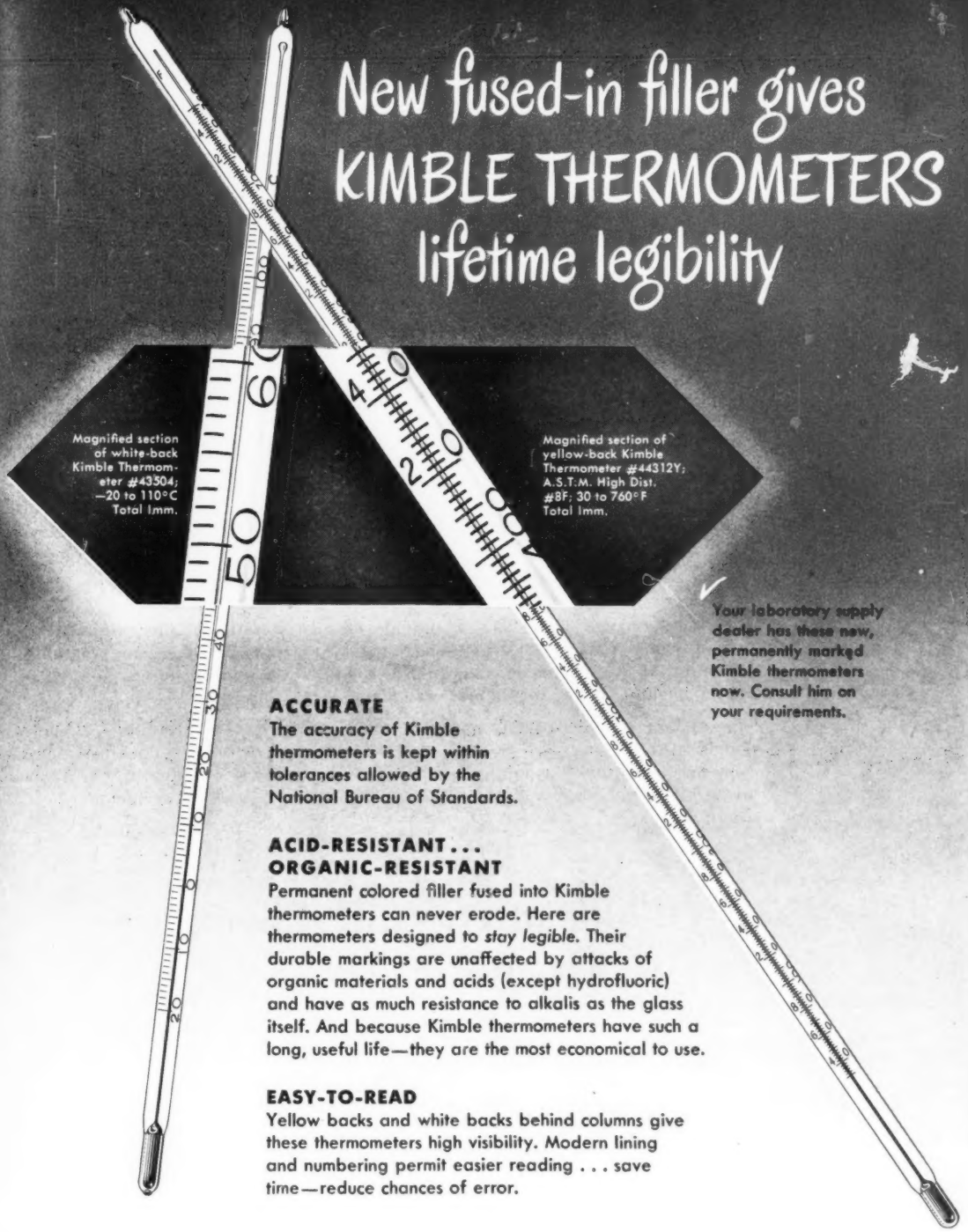

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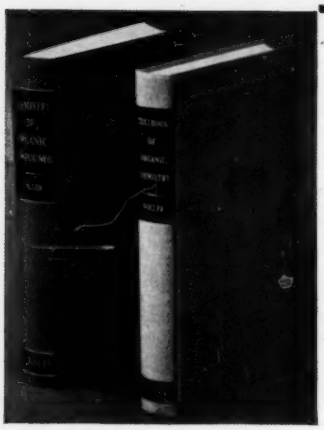

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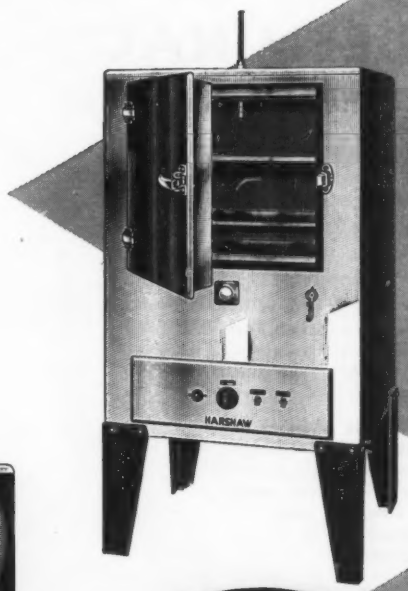


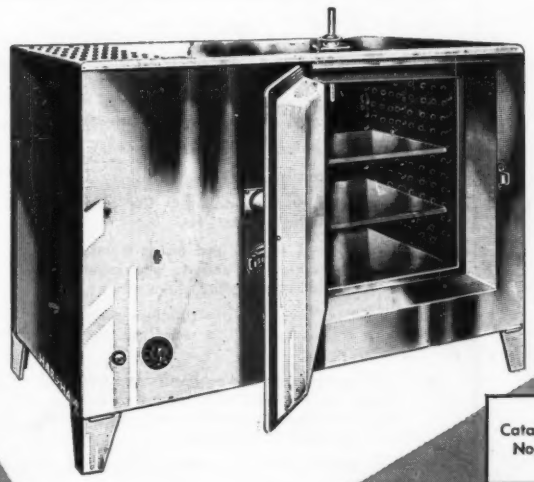

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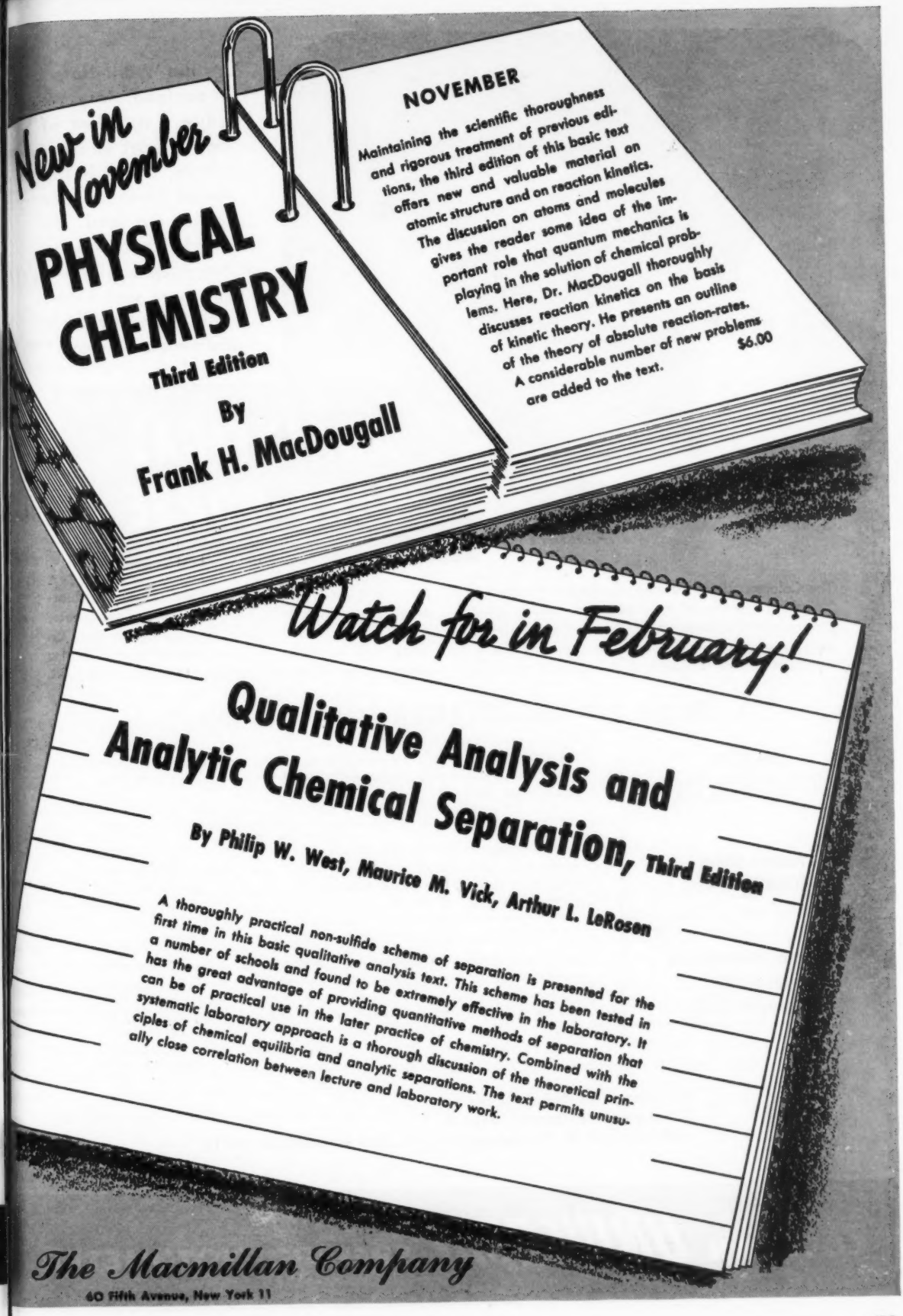
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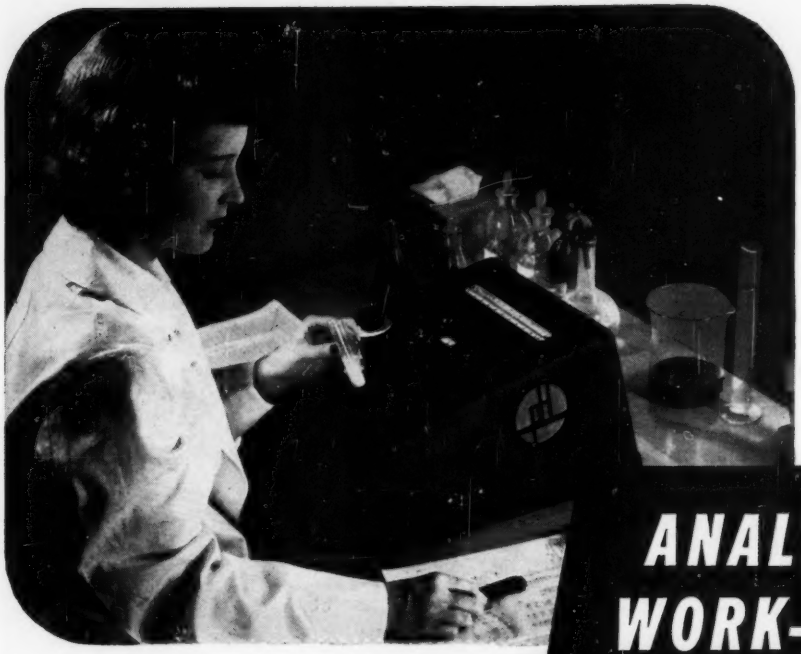

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***Gustav Kortüm***

(See page 2)

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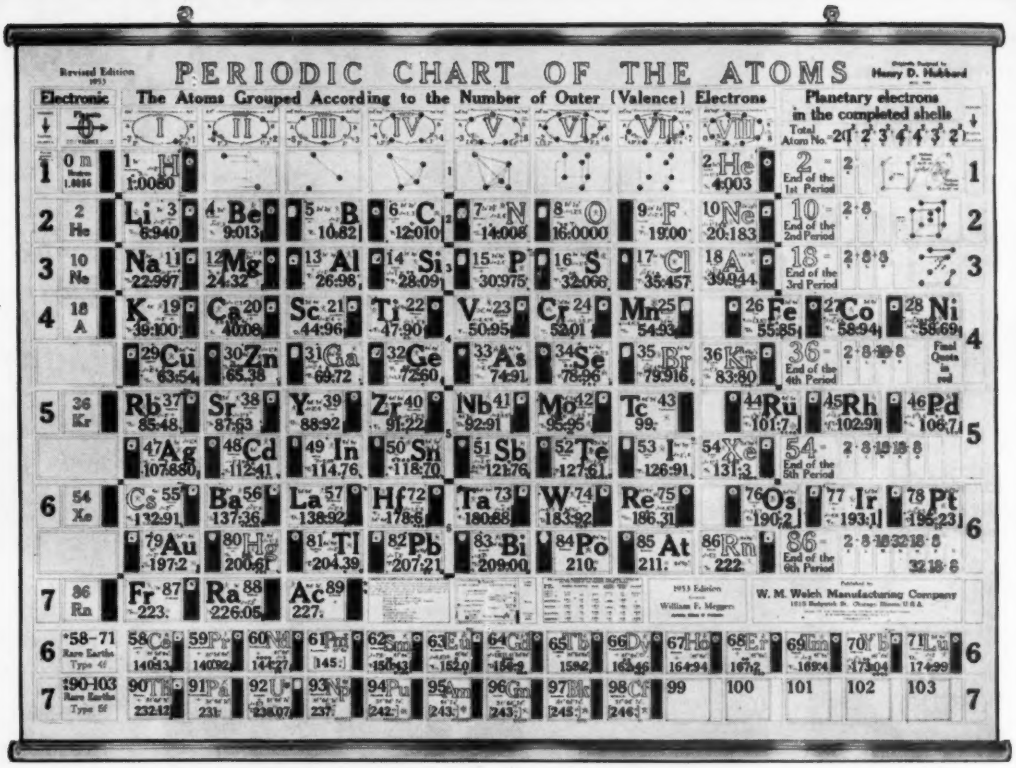


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# Editor's Outlook

THE concern over the shortage of scientific manpower is continually bringing to light new and old problems in chemical education. The necessity to develop and conserve every last bit of this precious assemblage of personnel is compelling us to examine the efficiency of every step in the process of selection and education. We must not miss any bets if we can help it.

The first step, in the secondary school, has already had some attention in these pages. The progress to the eventual goal should begin here, and often does. However, an interesting observation about steps is that they are not entirely discontinuous; motion does not completely stop between them, but one leads almost imperceptibly into the next.

And this leads me to my point, the correlation between the teaching of chemistry in the high school and that in the college. If all the pages that have been written on this subject were set end to end they would reach from here to some place far off. And if the heat in all the arguments thereon were put in one calorimeter it would boil the water out of it.

The fact is that there is too little relation between those who teach chemistry in the high school and those who do the job in college. The latter group often feel that the former are not chemists (sometimes true) and the former often resent the latter's sense of superiority and feel that they do not understand the real problem (also sometimes true).

This lack of relation contributes to an opinion which is far more prevalent than it should be—the opinion that high-school chemistry is a handicap rather than a help in college chemistry. Sometimes the opinion is expressed more factually (?): students in college chemistry who have had high-school chemistry get poorer grades than those who have had no preparation. Many conscientious and well-meaning college teachers have expressed such opinions, supposedly out of their own experience. It is surprising that people with scientific training should make such statements, based upon mere impressions rather than actual evidence. For, in every case with which I am familiar, an actual inspection of the facts has led to the opposite conclusion. I made such an inspection myself, in one case, and I know.

Why can't we stop this kind of slander? It is an insult either to the high-school teacher or to the student. Let us recognize the facts, be less pessimistic, and get together on a correlated program of chemical education to fill our needs.

# GUSTAV KORTÜM

**RALPH E. OESPER**
University of Cincinnati, Cincinnati, Ohio

GUSTAV (Ferdinand Albert) Kortüm, internationally known German physical chemist, was born on June 14, 1904, at Methling, Mecklenburg. He began his training in chemistry, particularly physical chemistry, at the Technische Hochschule in Karlsruhe in 1922. The doctorate (Dr.Ing.) was obtained under Bredig in 1928. Dr. Kortüm then was given a grant by the Deutsche Forschungsgemeinschaft and worked under Haber at the Kaiser Wilhelm Institut für physikalische Chemie at Berlin-Dahlem. Next he went to the University of Würzburg for further training under Ebert. From 1931 to 1936 he was assistant to von Halban at the University of Zurich. He habilitated as Privatdozent at the University of Tübingen in 1937, and in 1942 was made first extraordinary professor and then full professor and director of the Institut für physikalische Chemie, his present post.

Professor Kortüm's researches have touched many fields. The main currents of his interests may be gathered into four divisions:

(*a*) *Photoelectric precision photometry* (1930–44): development of the substitution method with alkali cells, precision 0.01 per cent of the extinction (1933); limits of the Lambert-Beer law and the optical constancy in ionic solutions (1935–36); development of a precision photometer for determining concentrations (1942); colorimetric analytical methods (1944–45).

(*b*) *Ultraviolet spectroscopy* (1936–51): development of a hydrogen point lamp (1936); detection of the action of dispersion forces between ions (1936–38); photographic methods for recording quantitative fluorescence spectra (1942); light absorption and mesomerism (1939–42); pressure broadening of the vibration bands of HCN (1943); photographic method for recording absorption spectra of powders (1947–51); optical study of the thermochromism of bianthrone (1950); interpretation of the relation between the constitution and fine structure in the absorption spectra of aromatic hydrocarbons (1951).

(*c*) *Electrolytes* (1936–51): study of the validity range of the Debye-Hückel limiting law (1934); titration method for the optical determination of dissociation constants of colorless acids (1949); conductance and transport measurements in mixed solvents, detection of selective solvation of ions (1950); dielectric and conductometric behavior of iodine in basic solvents (1951).

(*d*) *Thermodynamics* (1949–51): solubilities of iodine in solvent mixtures; detection and thermal dissociation constants of iodine complexes (1951); vapor pressure and boiling diagrams of binary and ternary liquid mixtures, development of new methods of measurement (1951); precision determination of vapor pressures and heats of mixing of apparently regular mixtures (1951).

These and other studies have of course resulted in an impressive list of papers from his laboratory. He has also authored the following books, whose titles alone reveal the breadth of his competence: "Neuere Forschungen über die optische Aktivität" (105 pages) 1932; "Das optische Verhalten gelöster Elektrolyte" (120 pages) 1935, reprinted at Ann Arbor 1945; "Elektrolytlösungen" (438 pages) 1941, reprinted at Ann Arbor 1945; "Kolorimetrie und Spektralphotometrie" (236 pages) second edition 1948; "Lehrbuch der Elektrochemie" (495 pages) 1948; "Einführung in die chemische Thermodynamik" (303 pages) 1949; "Textbook of Electrochemistry" (with J. O'M. Bockris) Volume I (351 pages) 1951; "Theorie der Distillation und Extraktion von Flüssigkeiten" (in press).

## THE ELECTRON AS AN ELEMENT

LET us again consider the combination of sodium with chlorine to form common salt. If it be conceded that salt differs from its solution only in so far as the mobility of the solution permits of transfer of ions, the transfer of an electron from the sodium to the chlorine must take place at the moment of combination. Symbolized, if we write E for electron and simplify the reaction, dealing for the moment with an atom and not with a molecule of chlorine, we have ENa + Cl = NaECl. Here the electron serves as the bond of union between the sodium and the chlorine.

If it be desired to form a mental picture of what occurs, let me suggest a fanciful analogy which may serve the purpose: it is that an electron is an amoeba-like structure, and that ENa may be conceived as an orange of sodium surrounded by a rind of electron; that on combination, the rind separates from the orange and forms a layer or cushion between the Na and the Cl, and that on solution the electron attaches itself to the chlorine in some similar fashion, forming an ion of chlorine. It will be noticed that the E fills the place usually occupied by a bond, thus: Na-Cl. It happens providentially that the bond and the negative sign are practically the same; Na-Cl may be supposed to ionize thus: Na(-Cl), the negative charge or electron remaining with the chlorine.—Sir William Ramsay, *J. Chem. Soc.*, **93**, 781 (1908).

# THE GENESIS OF THE METRIC SYSTEM and THE WORK OF THE INTERNATIONAL BUREAU OF WEIGHTS AND MEASURES

**HENRI MOREAU**
International Bureau of Weights and Measures, Sevres, France
*(Translated by Ralph E. Oesper)*

ON DECEMBER 10, 1949, the meter, the standard of length in the metric system, was 150 years old, and May 20, 1950, marked the 75th anniversary of the founding of the International Bureau of Weights and Measures. These two anniversaries, which were passed over practically unnoticed, recall important dates in the history of weights and measures, a history which to a great extent may be said to represent the history of civilization itself.

The history of the founding of the metric system is intertwined with that of the French Revolution of 1789. At various steps in the genesis of this system one encounters the names of eminent men of science and politics who played leading roles in this fateful period of French history. As for the Bureau of Weights and Measures, its creation was one of the consequences of the development of the metric system during the second half of the nineteenth century.

This paper will give the broad outlines of the origin of the metric system, that "enterprise whose result should belong some day to the whole world" (Talleyrand), and will describe the essential part of the work of that metrological institute of world-wide character, namely the International Bureau of Weights and Measures.

## DIVERSITY OF ANCIENT MEASURES

At all periods of social intercourse there has been a need for weights and measures so that commercial transactions can be carried on conveniently and honestly. This objective was far from attainment at the end of the eighteenth century, when a wide diversity of units produced inevitable confusion. Furthermore, there was considerable doubt as to the permanence of the standard weights and measures.

Without going into the detailed history of the ancient weights and measures, one dominant fact should be noted: the uniformity was illusory. The units varied, not only from country to country, and sometimes (as in France) from province to province, but even from city to city, and also according to corporation or guild. Of course, this state of affairs led to errors, frauds, and continual misunderstandings and disputes, to say nothing of the serious repercussions such a situation was bound to have on the progress of science. The multiplicity of names given to poorly determined units and the diversity in the multiples and submultiples of the principal measures increased the confusion.

To remedy this lack of uniformity and to obviate the consequent inconveniences, royal decrees relative to the unification and control of measures were issued at various times by the sovereigns, who, at the same time, hoped thus to increase their power over the whole country. Such decisions, which sometimes had real effects (Charlemagne, 789; Charles the Bald, 864, for instance) unfortunately did not outlive their sponsors.

The reform of the system of measures, which was neatly summed up in the motto "One King, one Law, one Weight, one Measure" occurring in more than one of the *cahiers* of the États Généraux (States General),[1] was constantly opposed by the interested resistance of the nobles, the influence of the guilds, and, in general, by all who profited by the prevailing disorder. Added to these hindrances was the innate indifference, if not the hostility, of those accustomed to their local units.

In Paris the principal units in use before the establishment of the metric system were the *Pied de Roi* (0.325 m.) for lengths and the *Livre poids de marc* (489.5 g.) for weights.[2] These two units were respectively represented by standards known as the *Toise du Châtelet* and the *Pile de Charlemagne*.

The Toise du Châtelet ( = 6 Pieds de Roi (1.949 m.)) was an iron bar that had been fastened in 1668 to the outer wall, at the foot of the staircase, of the Grand Châtelet.[3] At its ends were two notches or projections at right angles; a toise was supposed to fit precisely between them. This standard toise had served for the adjusting, among others, of the two famous toises, known as the *Toise du Pérou* and the *Toise du Nord*, which were used in measuring the arc of the earth's

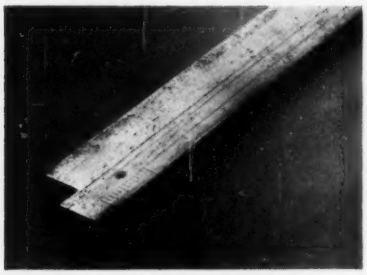
[1] The États Généraux was the general assembly of the whole French nation; the representatives were sent by the clergy, the nobility, and the third estate (the commoners). The first of these États Généraux convened at Paris in 1302.

[2] The subdivisions of these units were:

| | |
|---|---|
| Toise = 6 Pieds de Roi | Livre = 2 marcs |
| Pied de Roi = 12 pouces | marc = 8 onces |
| pouce = 12 lignes | once = 8 gros |
| ligne = 12 points | gros = 3 deniers |
| | denier = 24 grains |

Other units of length in common use were: the *aune* (ell) of 3 pieds, 7 pouces, $10^5/_6$ lignes (1.188 m.); the *lieue* (league) of 2.283 toises (4.45 m.); the *perche royale* of 3.666 toises (7.15 m.).

[3] The Grand Châtelet was the name of a fortress of ancient Paris which, along with the Petit Châtelet, guarded the heads of the two bridges giving access to the Cité. The Grand Châtelet was torn down in 1802.



(*a*)

(*b*)

**The Toise du Pérou or de l'Académie 1738.**

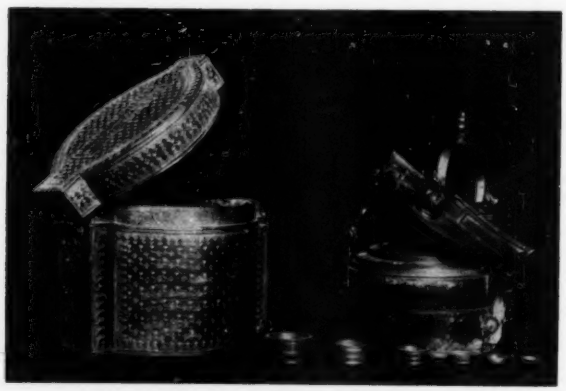
(*a*) One of the ends, where the lines showing the subdivisions in lignes (2.256 mm.) and pouces (27.07 mm.) can be seen.

(*b*) The inscription on the cover of the case. This ancient French standard of length is preserved at the Observatory in Paris.

meridian in 1735 to 1737 below the equator by Bouguer, La Condamine, and Godin, and in Lapland by Maupertuis and Clairaut. In 1766 the Toise du Pérou replaced the Toise du Châtelet as the legal standard of measures of length in France.

The Pile de Charlemagne, constructed in the last third of the fifteenth century, consisted of a series of 13 copper weights, nesting in each other; the ensemble weighed 50 marcs (12.2375 kg.).

Despite votes by the États Généraux, all attempts to impose the Parisian units on the entire French kingdom came to a halt more or less rapidly; the successive governments recoiled before the immense task. Though at present it is somewhat difficult to visualize the difficulties to which the confusion in the measures led at the time—a disorder which the English economist Arthur Young described as the "infinite confusion of the French measures, which passes anything one can imagine," and which aroused the indignation of Talleyrand because the "variety was ghastly"—enough has been said to depict the state of anarchy which prevailed with respect to weights and measures in France prior to the establishment of the metric system.



**The Pile of Charlemagne and Its Case, Which Bears the Inscription: "Poids original de la Cour des Monoyes." This Ancient French Standard of Weight is Preserved at the Musée du Conservatorie National des Arts et Métiers in Paris.**

It was necessary to wait for the great overturn accomplished by the French Revolution of 1789, whose great objective was the elimination of all traces of the feudal system and royalty, and for the influence of the French scientists, who realized the international import of such a forward step, before the problem could be put on a scientific basis and a complete reform brought about.

## CREATION OF THE METRIC SYSTEM

*Possible Bases of the New System.* The idea which guided the promoters of the reform of the weights and measures was to guarantee the invariability of the measures by relating them to a model taken from nature or to a standard whose magnitude was derived from natural phenomena. The new system would thus be based on a "natural universal unit," which would not belong to anyone and which could be adopted by all countries without arousing national jealousies.

When this problem was taken up in earnest, three propositions were advanced regarding the choice of the unit of length: a measured fraction of the length of an arc of meridian, or of the circle of the terrestial equator, or the length of a seconds pendulum.

The first proposition was a revival of that advanced in 1670 by the Abbé Gabriel Mouton, French astronomer and mathematician, who at the same time recommended a decimal division of the units. The idea of using the pendulum, which probably came from the Royal Society of London, had already been supported by Picard (1671), Huygens (1673), and Roemer. The real choice lay between the meridian and the length of the pendulum.

The project based on the pendulum, although attractive, was criticized at once. The length of the seconds pendulum depends on the intensity of the gravitational force and consequently is not the same at all points on the earth's surface. Moreover, the second, a unit of time, would enter into the definition of the unit of length.

Before proceeding farther with the study of the plan of reforming the system of weights and measures, the French authorities sought the cooperation of England to insure that the new system would have an international character. At this time the English were considering a reform of their own measures, and Sir John Riggs Miller had just proposed the length of the pendulum as the base (July, 1789). Accordingly, the time seemed eminently suitable for an *entente* in this matter between the Royal Society and the Académie des Sciences de Paris.

In March, 1790, Talleyrand, then bishop of Autun, laid before the Constituent Assembly a plan of the unification of weights and measures, likewise based on the length of the pendulum, and he requested England to collaborate with France in fixing the base of the new measures.

*The Adoption of the Meridian.* While awaiting the reply from the English, and after discussing the Talleyrand plan, the Académie des Sciences appointed a first commission, which adopted the decimal scale for all the divisions of weights, measures, and coinage (October 27, 1790).

A second commission, composed of Borda, Lagrange, Monge, and Condorcet, was charged with fixing the base of the unit of linear measure. Rejecting the length of the pendulum, for the reasons just given, this commission finally decided in favor of the quadrant of the earth's meridian, the ten-millionth part to be the actual unit of length. Since it was obviously difficult to consider the measurement of a quarter of the entire meridian, it was decided that they would limit themselves to measuring an arc extending between Dunkerque and Barcelona, the extremities of this arc of meridian, both at sea level, located to the north and south of the 45th parallel. This plan was adopted by the Assemblée Nationale on March 26, 1791, and the Académie immediately named the various commissions whose duty it would be to carry out the tasks necessary to the execution of this plan. Delambre and Méchain were placed in charge of the measuring of the arc of meridian, while Lavoisier and Haüy (later Lefèvere-Gineau and Fabbroni) were assigned the determination of the weight of a known volume of water from which to deduce the standard of weight.

*Attitudes of the English and the Americans.* The hoped-for cooperation of the English in the creation of the new system was not obtained. On December 3, 1790, shortly after the Riggs Miller project was placed before the House of Commons (April 13, 1790), the Duke of Leeds, Secretary for Foreign Affairs, replied to the Marquis de la Luzerne, the French Ambassador, that the British Government regretted that it could not accede to the proposals of the French Government, the arrangement being considered "impracticable."

As for the Americans, the reform of measures was also a matter then under consideration. In January, 1790, President Washington sent a message to Congress inviting that body to study the system of weights and measures. Secretary of State Jefferson proposed that a choice be made between two solutions: definition, simplification, and uniformization of the existing system of English units, or the establishment of a new system based on the seconds pendulum, with decimal multiples and submultiples of the fundamental unit taken equal to three-tenths of the pendulum's length.

Jefferson, though thoroughly enthused with the plan of seeing an invariable and universal standard adopted, nevertheless would not accept the meridian that was being supported by the Académie des Sciences de Paris, but adhered to the pendulum. He thought that the base of the new system should be a measurement that could be readily made in all countries; since the proposed meridional measurement could hardly be made anywhere other than between Dunkerque and Barcelona, France and Spain would thus have a monopoly on the checking of the unit of length.

This negative attitude was confirmed later when in 1795 Washington sent to Congress a communication from the Minister of the French Republic suggesting that the United States adopt the metric system of weights and measures. This proposal found little favor; a unit based on the ten-millionth part of the earth's quadrant was deemed less favorable from the point of view of its reproducibility than a seconds pendulum.

Thus, faced with the nonconcurrence of the most important foreign powers, the French proceeded alone toward the establishment of the new system, the system which "though conceived and created in France, will belong to all the nations."

**Charles-Maurice de Talleyrand-Périgord, Prince of Benévent (1754–1838). Bishop of Autun 1788–91, Member of the Constituent Assembly, then Diplomat, Noted Particularly for His Brilliant and Able Part in the Congress of Vienna (1814–15)**

*The Determination of the New Units.* Almost ten years elapsed between the deposition of the Talleyrand proposal (March, 1790) and the definitive fixing of the value of the new unit (*mètre*) in December, 1799. This interval may appear excessive; but it should not be forgotten that all the operations requisite to the determination of the units of length and weight were carried out while the Revolution was in full swing. This unsettled atmosphere seriously hampered the progress of the work. Nor were the scientists in charge of the operations spared: loyalty tests, arrest, confinement, and even condemnation to death—such was the fate reserved for some of them during this period of political unrest and disorder.

Obviously, not all the labors of these ten years can be discussed here; the essential features will be outlined briefly.

*Unit of Length.* The measurement of the arc of meridian was divided into two parts: the northern sector, extending from Dunkerque to Rodez, was confided to Delambre; the southern part, from Rodez to Barcelona, was intrusted to Méchain. This geodetic operation—for which Delambre and Méchain employed the *repeating circle* (recently invented by Borda) which permitted a precision of one second in measurements of angles—consisted essentially of triangulation measurements and determinations of latitudes and azimuths.

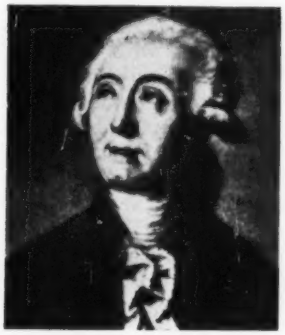
Jean-Baptiste Delambre (1749–1822), Astronomer

The Arc of the Meridian Measured by Delambre and Méchain Between 1792 and 1798

Pierre-Francois Méchain (1744–1804), Astronomer

This important work was interrupted several times for various reasons; in the course of its execution numerous incidents and adventures occurred with Delambre and Méchain as their unfortunate victims, such as arrests and revocations of their right of passage, damage to and destruction of their work. Among other happenings, the markers which they used for their observations excited the distrust of the people; the white cloths—the royal color and hence counter-revolutionary—which were at the ends of these markers made the two scientists and their assistants suspect in the eyes of some of the local authorities, even though the scientists were fully provided with passports, permits, and the other necessary authorizations.

Begun in June, 1792, the determination of the length of the arc of meridian was not entirely finished until June, 1798. The results of this operation, approved by a commission of French and foreign scientists, gave the distance from the pole to the equator as 5,130,740 toises, or for the length of the meter 3 pieds, 11.296 lignes.



Antoine-Laurent de Lavoisier (1743–94), Chemist

Louis Lèfevre-Gineau (1754–1829), Physicist and Man of Public Affairs

Jean Valentin Fabbroni (1753–1822), Italian Chemist and Engineer

*Unit of Weight (Mass).* All the plans for reform emphasized that there must be a connection between the unit of weight and that of volume, and consequently with that of length. This part of the work, of course, was taken up by the Académie des Sciences.

The assignment, entrusted in 1791 to the academicians Lavoisier and Haüy, was almost completed in August 1793, when it was taken over entirely by the academician Lefevre-Gineau, assisted later by Fabbroni, deputy from Tuscany. The latter two scientists determined the weight of a known volume of water by weighing successively in water and in air a hollow brass cylinder whose dimensions had been carefully determined. These data yielded the weight of a cubic decimeter of distilled water taken at its maximum density (4°C.) and weighed *in vacuo*.

The results of this determination, likewise approved by a commission made up of French and foreign scientists, gave, with respect to the Pile of Charlemagne, the value 18,827.15 grains, which was adopted as the weight of the new unit: the kilogram.

Once these two important results had been obtained, all the elements requisite to the establishment of the standards of units of length and weight were at hand.

It should be noted however that prior to the delivery of the definite figures for the measurement of the arc of meridian and the determination of the unit of weight, two decisions were taken:

(1) A provisional system of measures was created in 1792 and sanctioned on August 1, 1793; a first nomenclature of the units was decided on and a provisional meter of brass, constructed by Lenoir, was sent to the Committee of Public Instruction on July 6, 1795; the length of this meter, deduced from the old (1740) measurements of the earth, was 3 pieds, 11.44 lignes.

(2) A little later, the law of the 18th of Germinal year III (April 7, 1795) instituted the decimal metric system in France and fixed the nomenclature of the new units, a terminology that is still in use: *mètre* for lengths, *are* for areas, *litre* for capacities, *gramme* (later *kilogramme*) for weights (masses); an article of this law also stipulated that the meter, which had been adopted as the fundamental unit of the entire system of measures, should be traced on a platinum rule.

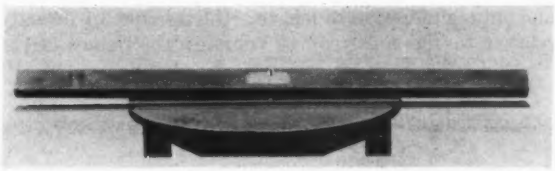
*The Construction of the Standards.* In conformity with the provisions of the law of the 18th of Germinal, the standard meter and kilogram were constructed to give material form to the units whose magnitude had just been determined.

For the meter there was prepared, not a line standard but instead an end standard, i. e., a standard on which the length was not marked by the distance between two lines but by the distance between its terminal faces. The standard consisted of a straight rule, with a rectangular section 25.3 × 4 mm., and made of agglomerated platinum.[4] This rule was compared with the toise by means of the comparator constructed by Lenoir.

For the kilogram a platinum standard was prepared in the form of a polished cylinder, whose height was equal to its diameter. Its weight was probably adjusted with the aid of the balance and the provisional weights used in the determination of the weight of a known volume of water.

[4] At that time platinum was obtained from spongy platinum produced by calcining ammonium chloroplatinate; the product was compressed, brought to white heat, and them hammered.

**This Medal Almost Put into Effect the Plan of Issuing a Medal Which Was to Be Struck in 1799 "To Transmit to Posterity the Occasion at Which the Metric System Has Been Brought to Perfection, and the Operation Which Served as Its Base."**



**The Mêtre des Archives and Its Case, Which Bears the Inscription:**
Mètre
Conforme à la Loi du 18 Germinal an 3
présenté le 4 Messidor an 7

This prototype meter and kilogram were presented by a delegation of the Institut de France to the Conseil des Anciens and Conseil des Cinq-Cents[5] on the 4th Messidor year VII (June 22, 1799) and then deposited at the Archives de la République, which accounts for the name *Mètre et Kilogramme des Archives* which has been attached to these standards. The law of the 19th

[5] The Conseil des Anciens and the Conseil des Cinq-Cents were assemblies that made up the Corps Législatif organized by the Constitution of the year III (1795).

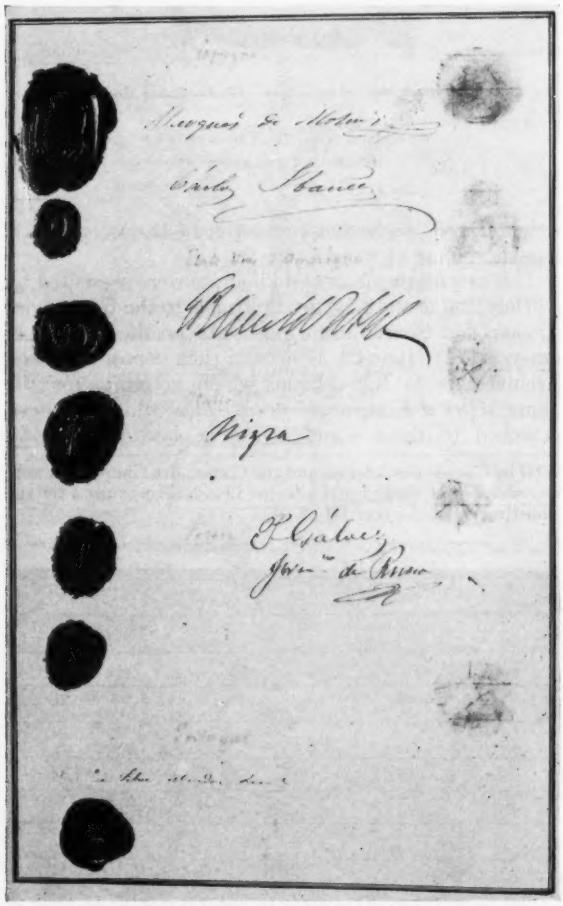
**The Kilogramme des Archives and Its Case**

Frimaire year VIII (December 10, 1799) finally assigned a legal value to them.

This brought to a close the gigantic plan of unifying the weights and measures, concerning which the illustrious Lavoisier—who took a leading part in all the preparatory labors of this reform until he went to the guillotine on May 8, 1794, during the Reign of Terror—could state: "Never has anything more grand and more simple, more coherent in all of its parts, issued from the hand of men."

## ADOPTION OF THE METRIC SYSTEM

The advantages of the simplicity and coherence of the metric system are widely recognized; a few words will suffice to recall its chief characteristics: First of all, it is entirely decimal, like the system of counting; the measures of area and volume are obtained by squaring and cubing measures of length; the weights are directly related to the measures of volume; the names of the multiples and submultiples are obtained by the simple addition of prefixes to the principal unit: kilo (k) = $10^3$; hecto (h) = $10^2$; deca (da) = 10; deci (d) = $10^{-1}$; centi (c) = $10^{-2}$; milli (m) = $10^{-3}$.



**Convention du Mètre (1875): One of the Pages of Signatures. The Third from the Top Is That of the American Plenipotentiary, Elihu Benjamin Washburne, Envoy Extraordinary and Minister Plenipotentiary of the United States to Paris.**

Despite the ease with which it is used, this system was not adopted immediately throughout the whole of France; its introduction was slow and difficult. The new system required a profound alteration in long established customs, and the various changes in the nomenclature re-enforced the opposition offered by the public.

The consular decree of 13th Brumaire year IX (November 4, 1800) re-establishing the old names of the measures (lieue, livre, once, perche, etc.), while retaining those of the meter and the decimal division, merely aggravated the situation by creating regrettable confusions: certain different units were found in effect to be bearing the same name. Then came the unfortunate imperial decree of February 12, 1812, authorizing, along with the legal system, the creation of measures called "usual" accommodated to the need of the people. For example, there was created a toise of 2 meters, a livre of 500 grams, a boisseau (bushel) of one-eighth hectoliter, etç., which were subdivided, according to ancient customs, into nondecimal units.

The reform had hardly been brought about before it found itself gravely menaced and the former anarchy began once more to reign among the measures. The resistance reorganized anew; besides satirical screeds and cartoons ridiculing the metric system, there were untoward incidents and even serious disturbances at various places. Immediate action was needed to safeguard the accomplished task.

The law of July 4, 1837, brought an end to this abnormal situation; it forbade, under the pain of severe penalties, the use of any weights and measures except those of the decimal metric system after January 1, 1840. The period of concessions, which had lasted a quarter of a century, was thus brought to a definite close, and the year 1840 marks the date of the beginning of the exclusive use of the metric system in France.

Becoming gradually known and appreciated in foreign countries, the metric system made rapid progress in the world, thanks to its simplicity and its logical and rational conception. Some of the Italian provinces adopted it at the beginning of the nineteenth century; in 1816 it was declared obligatory in the Low Countries; Spain accepted it in 1849. After 1860 the adoptions multiplied. In Great Britain, the law of July 29, 1864, authorized the use of the metric weights and measures concurrently with the imperial system; on July 28, 1864, the United States of America made an analogous decision. Despite its rejection of the metric system in 1795, the American Congress legalized the use of this system almost a century later by passing the Metric Act of 1886, declaring: "It shall be lawful throughout the United States of America to employ the weights and measures of the metric system; and no contract or dealing or pleading in any court shall be deemed invalid, or liable to objection, because the weights or measures

expressed or referred to therein are weights or measures of the metric system."

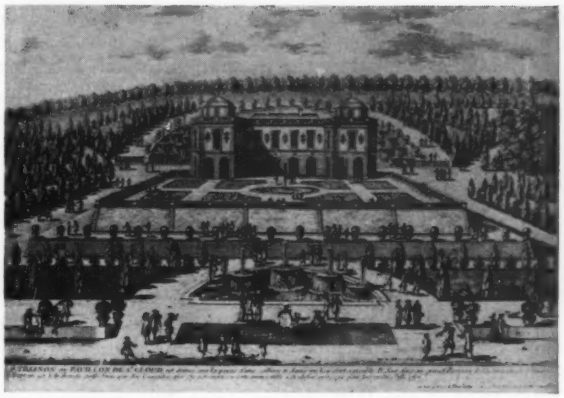
## THE INTERNATIONAL BUREAU

The first manifestations of the need for a world-wide unification of measures came to the fore on the occasion of the international expositions of London (1851) and Paris (1867). This thought was strengthened by the wishes uttered by various learned societies (Association Géodésique, Academies of Science of St. Petersburg, Paris, etc.), relative to the manufacture of new standards and the precise determination of their value in the metric system as based on the Mètre et Kilogramme des Archives in their actual contemporary condition. The international Geodetic Conference, held at Berlin in 1867, taking cognizance of the systematic differences that arose in the great European triangulations then in progress, recognized the need of fixing the common unit of measure for all the European countries; it also went on record as favoring the creation of an international bureau of weights and measures.

In response to these wishes, the French government in 1870 called together representatives of foreign countries. Twenty-four states responded to this invitation and their delegates constituted the *Commission Internationale du Mètre*. Interrupted by the Franco-Prussian war of 1870, the work of this body was resumed in 1872, with the participation of delegates from 30 countries, including 12 from the Western Continent. About 40 resolutions were passed dealing with the preparation of new prototypes, and the creation of an international bureau of weights and measures was recommended to the interested governments.

The members of this international commission, composed entirely of scientists, had no authority to commit their governments; it was only some years later that the establishment of this international bureau was officially sanctioned by the Conférence Diplomatique du Mètre, held at Paris in 1875 and which, through the signatures of the plenipotentiaries of 28 states, resulted in the *Convention du Mètre* (May 20, 1875). By this Convention (modified by the additional Convention of October 6, 1921) the signatory states bound themselves to set up and maintain at common expense a scientific and permanent International Bureau of Weights and Measures; its seat to be at Paris, the birthplace of the metric system.

The initial essential mission of this international bureau was to construct and preserve the definite standard meter and kilogram, to compare with them the national standards which were to be furnished to the various countries, and to improve the procedures of measuring in order to advance the progress in all fields of metrology. In proportion to the accomplishment of this program, the activity of the Bureau has been oriented toward the study of various metrological problems and of physical quantities entering into the accuracy of the measurements. During recent years, the assignments of the Bureau have also extended into the field of electrical and photometric units.



**The Trianon or Pavillon de Saint-Cloud at the End of the Seventeenth Century**

## THE PAVILLON DE BRETEUIL

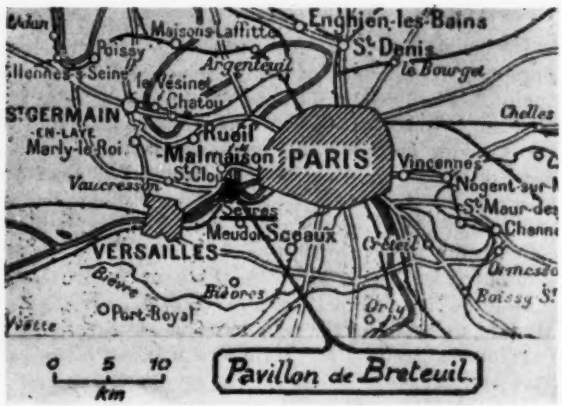
The choice of the site where the International Bureau of Weights and Measures would be located was finally decided in favor of the estate of the Pavillon de Breteuil, a peaceful spot, free of vibrational disturbances. This property was graciously put at the disposal of the International Committee of Weights and Measures by the French Government; with an area of 25,500 m., it thus constitutes a tiny international enclave within French territory.

Situated on the edge of the Parc de Saint-Cloud, close to the road from Paris to Versailles, and near the Manufacture Nationale de Porcelaine de Sèvres, the Pavillon de Breteuil is a structure with an historical past, built on the site of an ancient royal property.

Towards the middle of the seventeenth century Louis XIV, proprietor of this estate, presented it to his only brother, the Duc Philippe d'Orleans. The latter made some important improvements. The gardens were laid out by Le Nôtre—the famous landscape artist, to whom is due, among others, the magnificent gardens at Versailles—and this new estate became the Trianon de Saint-Cloud, a dependency of the Château

**The Pavillon de Breteuil (Present Appearance). *To the Left:* the Laboratories. *To the Right:* Offices, Assembly Hall, Library, Residences**

of this name that was destroyed during the war of 1870. In 1743 the Trianon de Saint-Cloud made way for a new pavilion erected by the Baron de Breteuil, Minister of the King's Household, thus giving this building the name Pavillon de Breteuil, which it has borne ever since. Badly damaged during the French Revolution, the Pavillon was restored by Napoleon I, who for a time gave it the name Pavillon d'Italie. Among those who lived in this rural retreat at that time were the Empresses Joséphine and Marie-Louise; the Queen of Naples, sister of Napoleon I; and Queen Hortense and her children, including the future Napoleon III. After the fall of the Empire the Pavillon de Breteuil was occupied by the Prussians, under Blücher, who did considerable damage to the property. Abandoned during the period of the Restoration (1814–30), the residence was restored by Napoleon III, who lodged his cousin Princess Mathilde, daughter of Jérôme Bonaparte, King of Naples, there in 1848. The Grand Duchesses of Baden and Marie of Russia also resided at the Pavillon.




**Geographical Location of the Pavillon du Breteuil.** ***Longitude:*** **2°13′14″ (2.467 grades) east of Greenwich.** ***Latitude:*** **N 48°49′45″ (54.255 grades).** ***Altitude:*** **65.9 m.**

Just at the time it was planned to install a laboratory of celestial physics at the Pavillon, the Franco-Prussian War of 1870–71 was declared. During the siege of Paris the Pavillon de Breteuil once more sustained considerable damage. Consequently the property was in a rather run-down condition when it was turned over to the Comité International des Poids et Mesures on October 4, 1875. The latter made the necessary repairs, and a new building, designed to house the scientific apparatus, was finished in 1878. Many years later (1930), because of the extension of the duties of the Bureau, some new laboratories were built with funds supplied by the Rockefeller Foundation.

During the second World War the bombardments of the Paris region spared the Pavillon de Breteuil entirely. Only the air attacks, aimed at the Renault factories at Boulogne-Billancourt, especially that of March 3, 1942, did some damage to the buildings; fortunately, the scientific instruments escaped injury.

This, in brief, is the history of the Pavillon which, after having sheltered so many historic personages and having witnessed sumptuous fetes, is now the international sanctuary of the standards of the metric system.

## OPERATION OF THE BUREAU

From the point of view of organization, the supreme authority governing the Bureau emanates from the General Conference of Weights and Measures, made up of delegates from all the countries belonging to the Convention du Mètre.[6] This Conference normally meets every six years; the tenth is scheduled for 1954. The opening session, in the great Salon de l'Horloge of the Quai d'Orsay, is presided over by the French Minister of Foreign Affairs; the working sessions, headed by the President on duty of the Académie des Sciences, are held at the Pavillon de Breteuil. The duty of the General Conference is to discuss and initiate steps leading to the propagation and improvement of the metric system throughout the world, and also to sanction new fundamental metrological determinations, and to approve of the various scientific and administrative decisions that have arisen between the meetings.

The decisions of the General Conference are put into effect by a permanent International Committee of Weights and Measures, which controls the functioning and the management of the International Bureau. This committee meets every two years at the Pavillon. At present, it is composed of 18 members at the maximum—scientists or technologists of all nationalities—whose election is submitted to the General Conference for ratification. Between sessions of the Conference, the Committee fills by election any vacancies in its membership arising from deaths or resignations. It is understood that countries with large populations have a permanent seat, the other seats are assigned in rotation to the smaller nations. The present chairman of the International Committee is British (J. E. Sears); the secretary is a Belgian (M. Dehalu); the American member is E. C. Crittenden, of the National Bureau of Standards.[7]

The International Bureau, composed of a scientific, administrative, and technical personnel (17 in all at present) who may belong to any nationality, is headed by a Director (at present a Swiss, Ch. Volet), named by

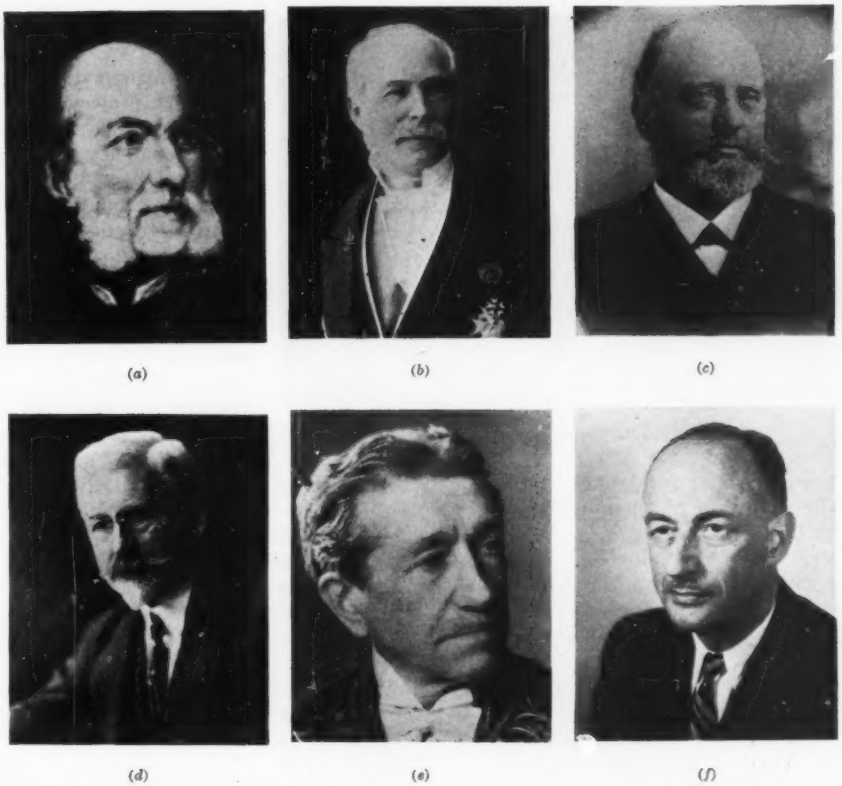
[6] At present, 33 states belong to the Convention du Mètre; they are: Argentina, Australia, Austria, Belgium, Bulgaria, Canada, Chile, Czechoslovakia, Denmark, Eire, Finland, France and Algeria, Germany, Great Britain, Hungary, Italy, Japan, Jugoslavia, Mexico, Netherlands, Norway, Peru, Poland, Portugal, Rumania, Siam, Spain, Sweden, Switzerland, Turkey, United States of America, U.S.S.R., Uruguay. It should be noted that this list does not include all the countries that have adopted the metric system, but only those—metric or not—that are adherents of the Convention du Mètre.

[7] The preceding American members of the Comité were: J. E. Hilgard (1875–87), Director of the Coast and Geodetic Survey; B. A. Gould (1887–95), Professor at Harvard University; A. A. Michelson (1897–1905), Professor at the University of Chicago; S. W. Stratton (1905–31), President of the Massachusetts Institute of Technology; A. E. Kennelly (1933–39), Professor at Harvard University.

secret ballot cast by the International Committee, in which he has a vote *ex officio*. One of the regulations appended to the Convention du Mètre specifies that the President, the Secretary of the Committee and the Director of the Bureau shall be of different nationalities.

The expenses of the Bureau are guaranteed by contributions paid by each state belonging to the Convention du Mètre. The annual subscription, set at 175,000 gold francs (about $57,000) by the ninth general Conference, is apportioned according to the population of each country, with maximum limits of 15 per cent (countries of high population) and minimum of 0.5 per cent (countries with low population) of the total sum.

All of the countries which contribute to the support of the Bureau are co-proprietors of its furnishings; they are entitled to obtain standards of the first order and have the right to request metrological determinations and studies *gratis*. However, along with these privileges, the chief advantage is cultural and moral. The desire to collaborate in the advancement of metrological science is the motive that leads the nations to belong to the Convention du Mètre; by this adhesion they are acknowledging the duty of every cultivated country to participate in a task of world-wide progress, from which they themselves will benefit.



(*a*) (*b*) (*c*)

(*d*) (*e*) (*f*)

**Directors of the International Bureau of Weights and Measures. (*a*) Gilberto Govi (1826–89), Italian physicist. Director 1875–77. (*b*) Ole Jacob Borch (1818–89), Norwegian mathematician. Correspondent of the Institut de France. Director 1879–89. (*c*) J. Rene Benoit (1844–1922), French. Correspondent of the Institut de France. Director 1889–1915. (*d*) Charles Èdoudard Guillaume (1861–1938), Swiss. Correspondent of the Institut de France. Nobel Prize in physics (1920). Director 1915–36. (*e*) Albert Perard (1880), French. Member of the Institut de France. Director 1936–51. (*f*) Charles Volet (1895), Swiss. Present director.**

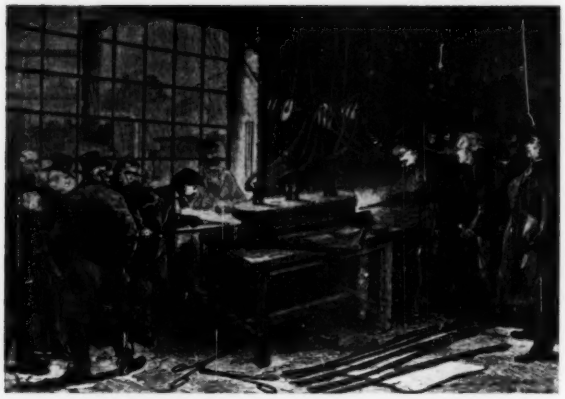
## THE INTERNATIONAL PROTOTYPES

In compliance with one of the articles of the Convention of 1875, the Bureau first of all took steps to assure the unification of measures by the construction and the determination of the international meter and kilogram, and also of copies to be distributed to all the countries that had requested them.

Pursuant to resolutions of the Commission Internationale du Mètre, study and research committees were organized in 1872 to produce the new standards and perfect the methods of comparing them. The details of all of these studies from 1872 to 1880 will not be given here. It will only be recalled that it was decided, among other things, that: (1) the international meter would be a line standard because of the advantages this construction offers with respect to comparisons and preservation; (2) the metal used for the standards would be an alloy composed of 90 per cent platinum and 10 per cent iridium; (3) the transverse section of the meter bars would be the X-shape computed by H. Tresca; (4) the value of the standard meter and kilogram would be deduced from that of the Mètre and Kilogramme des Archives in their existing condition.

The name of the French chemist H. Sainte-Claire Deville (1818–81) remains linked with the choice of platinum-iridium for the manufacture of the standards. This alloy is especially suitable because of its inalterability, homogeneity, hardness, high coefficient of elasticity, not too great expansibility (0.0086 mm./m./degree C.), and its ability to take a high polish.

The casting of a considerable quantity of platinum-iridium of well-defined composition was always a difficult task at that time. After many test castings, of which two were made in the presence of the French presidents, A. Thiers (May 6, 1873) and Maréchal de Mac-Mahon (May 1, 1874), these difficulties were all but overcome and a definitive casting of 250 kg. of this metal was made on May 13, 1874, at the Conserva-



Casting of the "Alliage du Conservatoire" in 1874

toire National des Arts et Métiers in Paris, furnishing the supply of platinum-iridium known as the *Alliage du Conservatoire* or *Alliage de 1874*. After analyses had shown that this alloy contained small amounts of impurities, the Johnson Matthey Company of London was commissioned to cast a new and purer alloy (*Alliage Johnson-Matthey*) from which 30 metric bars were drawn.

The X-shaped section of the bars permits the engraving of lines on the surface of neutral fibers laid bare along the entire length of the bar, and thus makes the length of the standard independent of the effects of bending due to the action of its own weight, no matter how the bar is supported. For a limited quantity of material, this profile has the added advantage of possessing a high moment of inertia, which measures the resistance of the bar to deformations. (Actually, an

Prototype Meter and the Various Parts of Its Shipping Case

X-shaped meter rule, supported at its ends and bearing a mass of 40 kg. at its center, does not suffer any permanent deformation.) This advantage is considerable if one takes into account the monetary value of the precious metal entering into the manufacture of a meter bar, whose mass is of the order of 3.3 kg.

After rejecting glass, quartz, and gold, the same alloy was adopted for the standard kilograms as was used for the meters.

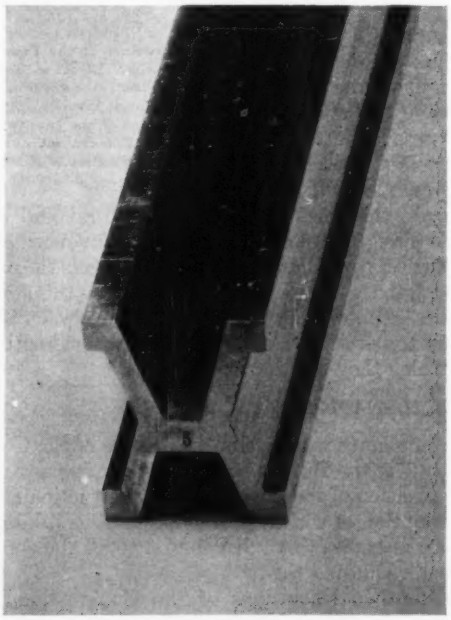
The form of the Kilogramme des Archives was retained: a perfectly polished cylinder, the diameter (39 mm.) equal to the height, with the edges very slightly rounded.

Once the meters had been constructed, the Bureau proceeded, in 1888, to an important intercomparison of the bars, to which had been added a provisional prototype compared directly with the Mètre des Archives. A similar project was carried out for the kilograms, which were referred back to the weight *in vacuo*.

The comparisons finished, the international prototypes of the meter and kilogram were selected from among the standards whose values were closest to that of the Mètre and Kilogramme des Archives, respectively. These prototypes and their "*témoins*" (companion replicas) are preserved in the vaults of the Pavillon de Breteuil, 8 meters under ground; three keys, held by three different persons (the President of the International Committee, the Directeur des Archives de France, the Director of the International Bureau) are required to open this vault. Consequently, the international prototypes are not visible to the visitors who come to the Pavillon de Breteuil; for them are provided "factitious standards," which they may examine and handle without risk of damage to the actual standards.

During World War II, the international prototypes were not taken from the Pavillon de Breteuil; only the *témoins* and the working standards were temporarily moved (May to September 1940) to Brittany and the Vendée.

The first General Conference of Weights and Measures (September, 1889) approved the results of this



**End of a Prototype Meter Identical with the International Meter**

Note the specular polished region on which is traced a group of three lines 0.5 mm. apart, the middle one, with its analogue at the other end, defining the length of the prototype. Two longitudinal lines about 0.2 mm. apart—not visible on the photograph because of the angle of illumination—cut across the three lines and thus outline their useful region. The X-shaped section is inscribed in a square of 2 cm. on the side. The total length of the meter rules is about 102 cm.; the width of the lines is around 5 $\mu$.

important work and then proceeded to distribute, by lot, the national prototypes among the various countries. It was thus that copies 21 and 27 of the meter and numbers 20 and 4 of the kilogram were alloted to the U. S. A.; they are preserved at the National Bureau of Standards, Washington, D. C. Likewise, at this time, approval was given to new definitions of the meter and kilogram, namely: The meter (or the kilogram) is the length at 0° C. (or the mass) of the international prototype in platinum-iridium, deposited at the Pavillon de Breteuil at Sevres.[8]

These definitions thus confer an agreed character on the metric system; it had in fact been difficult to maintain rigorously the original definitions of the meter and the kilogram, which would have led to new values for the standards each time the quadrant of the earth's meridian or the mass of the cubic decimeter of water is redetermined.

The permanence of the unit of length therefore now depends on the stability over the years of a platinum-iridium bar. This stability has been confirmed up to now, within the limits of the precision in the comparisons of the line standards, with the help of *témoins* associated with the international meter. In addition to the three companion bars, likewise constructed of platinum-iridium, two other *témoins* of a different nature have been sought: a wave length of light and a material in the crystalline state. Hence, at present, the wave length of the red line of cadmium and a series of plane-end standards constructed from Brazilian quartz permit the checking of the permanence of the standard of length through the constancy of the relationship of these three magnitudes. (The wave length of the red line of cadmium, measured as a function of the meter on nine occasions between 1892 and 1940 in various foreign laboratories, gave results all lying within $\pm 2 \times 10^{-7}$ of the mean value.)

[8] The seventh General Conference of Weights and Measures (1927) added some precisions to the definition of the meter, which now reads as follows: The unit of length is the meter, defined as the distance, at 0°C., between the axes of the two median lines traced on the platinum-iridium bar deposited at the International Bureau of Weights and Measures, and declared Prototype of the meter by the First General Conference of Weights and Measures, this rule being subjected to the normal atmospheric pressure and being supported by two rollers of at least one centimeter in diameter, situated symmetrically in a same horizontal plane and at the distance of 571 mm. from each other.

It should be noted that the International Meter, like the Mètre des Archives from which it was copied, is about 0.2 mm. shorter than the ten-millionth part of the quadrant of the earth's meridian, original definition of the meter. The same is true of the International Kilogram, which exceeds by 0.028 g. the mass of the decimeter cube of pure water, taken at its maximum density, original definition of the kilogram (see below).

**The International Kilogram. In the Foreground, the Holder Used for Handling the Standards**

**The Storehouse of the Metric Prototypes. The International Kilogram, Under Its Triple Glass Bell Jar, Surrounded by Its *Témoins*. In the Metal Cases, the International Meter and Its *Témoins***

It is more difficult to check the stability of the international kilogram because at present there is no available "natural" reference permitting such control. It is only the constancy of the differences between the international kilogram and its replicas, likewise made of platinum-iridium, that testifies to the permanence of the unit of mass. To guarantee the best possible conservation of this unit, the International Kilogram has been used on only two occasions (1889 and 1946) since its construction, with the hope of reducing to a minimum the inevitable loss of material that accompanies use.[9]

The stability of the platinum-iridium standards of length and mass is clearly shown by the following comparison of the original values (1889) of the American primary standards and those found at the most recent of the periodic verifications.

| | *1889* | *1922* | *1948* | *Difference* |
|---|---|---|---|---|
| Meter No. 27 | 1 m. − 1.49 $\mu$ | 1 m. − 1.48 $\mu$ | | +0.01 $\mu$ |
| Kilogram No. 20 | 1 kg. − 0.039 mg. | | 1 kg. − 0.019 mg. | +0.020 mg. |

## THE YARD AND THE POUND

The foregoing discussion of the characteristics of the standards of the metric system leads logically to a like consideration of the yard and the pound, *i. e.*, the bases of the British system of measures—units which incidentally do not have the same value in Great Britain and the United States— and their relation to the metric units.

*Great Britain.* The ancient yards, the "Iron Ulna" from the reign of Edward I (1239–72), the one made in 1496 during the reign of Henry VII which served until 1588, and the one established under Queen Elizabeth I, which was used from 1588 to 1824, were all end standards.

In 1760 Bird constructed a yard which was recognized as the legal standard by an Act of Parliament in 1824; this line standard was lost when the Houses of Parliament burned in 1834. The Bird standard had been related, in case of loss, to the length of a pendulum beating seconds at the latitude of London *in vacuo* and at sea level. However, this relationship was abandoned when the standard yard was remade, since the Kater measurements of the length of the pendulum were known to be unreliable because of errors, and the new yard was referred back to the old standard.

The metal chosen for the new standard was a bronze alloy containing 16 parts of copper, 2.5 of tin, and 1 of zinc (Baily's metal). Several rules were constructed and compared with ancient scales that had been verified against the 1824 yard. One of these rules was selected to be the standard of length at 62° F. (16.66° C.), and became the *Imperial Standard Yard.* Legalized by an Act of Parliament in 1855, this standard is now preserved at the Standards Department of the Board of Trade in London.

The Imperial Standard Yard, as well as its five Parliamentary Copies, is a line standard in the form of a bar 38 inches long (96.5 cm.) with 1 inch (25.4 mm.) square cross section; at one inch from each end there is a cylindrical cavity, 0.5 inch (12.7 mm.) deep, with a gold plug at the bottom on which are traced the lines defining the length of the standard.

The ancient pounds were replaced in 1844 by a platinum standard, the *Imperial Standard Pound.* This, like the four Parliamentary Copies, is in the form of a cylinder 1.35 inches (34.3 mm.) high and 1.15 inches (29.2 mm.) in diameter. This standard also is kept at the Board of Trade.

The legal relationships of the British units to the metric units are those approved in May, 1898:

$$1 \text{ yard} = 0.9143992 \text{ meter}$$
$$1 \text{ pound} = 0.45359243 \text{ kilogram}$$

The latest comparisons of the standard yard (1947) and the pound (1933) with the standard meter and kilogram gave:

$$1 \text{ yard} = 0.9143975 \text{ meter}$$
$$1 \text{ pound} = 0.453592338 \text{ kilogram}$$

which confirms a progressive shortening of the Imperial Standard Yard of the order of 2 parts in a million (1.7 $\mu$) in 52 years. A smaller ($2 \times 10^{-7}$) change, in the sense of a diminution, has likewise been observed in the Imperial Standard Pound.

*United States of America.* The situation regarding the system of weights and measures in the United States is rather peculiar: The metric system, which is employed almost exclusively in scientific work, has been legalized, whereas the system which is used in all daily transactions has never been officially approved in a formal manner.

The United States does not have any *legal* material standard yard or pound. These two units are directly related to the international meter and kilogram, as stated by the Mendenhall Order (1893): "The Office of Weights and Measures with the approval of the Secretary of the Treasury, will in the future regard the international prototype meter and kilogram as fundamental standards, and the customary units, the yard and the pound, will be derived therefrom in accordance with the act of July 28, 1866."

The relations of the U. S. A. yard and pound to the meter and kilogram are:

$$1 \text{ yard (U. S. A.)} = \frac{3600}{3937} = 0.91440183 \text{ meter}$$
$$1 \text{ pound (U. S. A.)} = 0.453592428 \text{ kilogram}$$

It is apparent that the U. S. A. yard is longer than the present Imperial yard by about four-thousandths of a millimeter (4.3 $\mu$) and that the U. S. A. pound is about 0.1 mg. heavier than the present Imperial pound.

[9] Since the area of the base of the platinum-iridium kilogram is about 12 cm.$^2$, the removal of 0.1 mg. of metal would only require that a layer four-millionths of a millimeter (0.004$\mu$) be worn away over the entire surface of the base. Obviously, certain precautions are indispensable when the standards are handled.

This anomalous situation of the different values of the English and American standards has not escaped the notice of the metrologists of the two countries. Therefore, as a consequence of the proved instability of the English yard and pound, it has been proposed that the standards of length and mass of the imperial system be defined in terms of the international meter and kilogram by a fixed relation which, if adopted simultaneously by the United States, would result in agreement in the units of these two countries.

Canada has recently set an example along this line; the Canadian yard and pound have been given the legal values:

1 yard (Canadian) = 0.9144 meter
1 pound (Canadian) = 0.45359243 kilogram

## ACTIVITIES OF THE BUREAU

Limited at the start to a well-defined and relatively narrow program, the activities of the International Bureau have progressively extended into various fields. All of these studies cannot be examined here, even briefly; reference can merely be made to the many articles in the scientific and technical press, or the papers and notes contained in the 21 volumes of the "Travaux et Mémoires" of the Bureau and in the *Procès-Verbaux* of the International Committee. Leaving aside the studies on barometry, hygrometry, the construction of prototype standards of the mercury ohm, the resistance of mercury, the expansibility of solids and liquids, the density of water, the mass of a liter of air, the standards with plane and spherical ends, the methods of calibrating divided rules and series of masses, the elasticity and deformation of solids, the metrological properties of brasses, the thin layers and the oxidation of aluminum, etc., it will be possible to review only the principal studies carried out at the Bureau and those which constitute the essential part of its present activity.

*Lengths and Masses.* The periodic verification of the national meters and kilograms is one of the essential tasks of the Bureau. These comparisons, though they may be elementary in principle, represent a body of important work in view of the care applied to these measures and the number of observations they entail. Thus, a simple example, such as the comparison of three rules in all possible combinations and relative positions, requires 24 series of comparisons, carried out usually by two or three observers, or even four when national prototypes are involved.

With a view to increasing the precision of the measurements, studies have been made of improvements to be applied to measuring instruments, to methods of observation, and to the standards themselves. Along this line, notable progress has resulted from the researches of Ch. Volet through the use of micrometric microscopes, which can be revolved a half-turn on their vertical axes and thus allow the elimination of errors, sometimes quite significant, that hitherto could not be avoided. Certain prototype meters, whose markings did not provide sufficiently accurate settings, have been re-engraved with special attention to the correct edging of the lines, an important point that was not kept sufficiently in view when the rules were originally engraved. Repeated cleaning of the markings produces a change in the appearance of the lines. These modifications are the origin of certain abnormal variations in length observed in certain prototypes whose defective lines have doubtless been altered in form.

These improvements make it possible to compare the 1-meter standards with a precision of 0.1 $\mu$, *i.e.*, with a relative accuracy of one ten-millionth ($10^{-7}$), a limit slightly exceeded with standards that have very regular markings. It should also be pointed out that the recent development of the micrometric photoelectric microscope, devised by the Société Genevoise d'Instruments de Physique, adds a new considerable increase of the precision in the measurement of line standards.

An important series of comparisons of mass standards was made between 1946 and 1951. The international kilogram, its six *témoins*, two working prototypes of the International Bureau, and about 30 national prototypes were included in these measurements. The importance of this study is apparent from the fact that more than 300 weighings—at the rate of one per day—were made by A. Bonheure, who was in charge of this periodic verification.

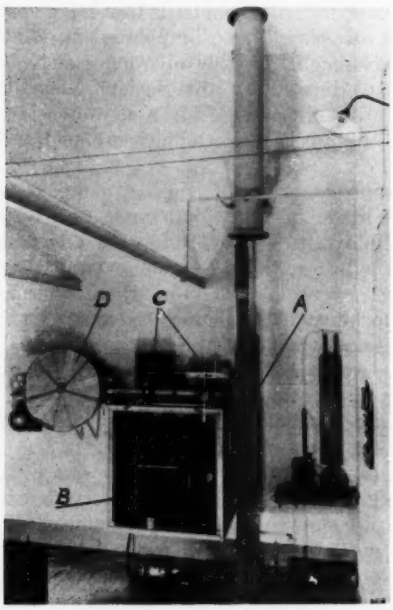
These determinations have led to a systematic study of the methods of cleaning weights; it was found in fact that the method of cleaning precision weights may have a significant effect on the observed mass. The investigation showed that the most efficacious method is a jet of doubly distilled water vapor. (The importance of cleaning is evident if it is remembered that a 1-m$\mu$ film of moisture over the entire surface of a platinum-iridium kilogram would change its mass by 0.01 mg.)

The highest precision in measurements is obtained in weighings; when comparing two 1-kg. weights, the best balances permit a precision of the order of one-hundredth of a milligram, or a relative value of one-hundredth of a millionth ($10^{-8}$). (This precision has even been exceeded with the new balance of the National Physical Laboratory of England, where several thousandths of a milligram have been approached.)

The first-order primary standards of platinum-iridium are of course very expensive; they are used only as prototypes. The standards of the second order (working standards of the metrological laboratories and precision industrial standards) are constructed of less costly materials. Studies along this line were carried on at the Bureau by Ch. Ed. Guillaume with ferronickels and led to the discovery of the unknown properties of certain of these metals, notably *invar* (an iron alloy containing 36 per cent of nickel, with an extremely low coefficient of expansion); *elinvar* (54 per cent Fe, 36 per cent Ni, 10 per cent Cr, which has a zero coefficient); *anibal* (a nickel steel, used for compensating balance wheels of chronometers); *platinite* (a

ferronickel containing 46 per cent Ni, whose expansibility is close to that of platinum); *baros* or *nichrome* (an amagnetic ferronickel containing 9 per cent Cr and 2 per cent Mn); the alloys containing from 42 to 58 per cent of nickel, whose expansibility is near that of the ordinary glasses or steel. All of these alloys have found application not only in metrology but also in industry.

The stainless steels, used for the construction of standards of length and mass, have also been studied with respect to their metrological properties.




**Setup (1951) for Determining "g" at the Pavillon de Breteuil**

*A*. Arrangement for the fall of the graduated rule. *B*. Apparatus for producing discharge sparks from a condenser (stroborama). *C*. Vibrating quartz regulating a light beam (about 35,000 cycles/sec.). *D*. Drum film-holder on which is recorded simultaneously the graduations of the rule during its fall and the chronometric track

Shortly after its founding the Bureau made a study of geodetic standards. The Jäderin method for the measuring of bases with the aid of stretched wires was brought to a high degree of precision by using geodetic wires of invar (wires 1.65 mm. in diameter, 24 m. long, provided at each end with a scale divided into millimeters, and used under a tension of 10 kg. force, or 98.1 newtons). Many geodetic wires are sent to the Pavillon de Breteuil by the various geographic services and their standardization is one of the important functions of the Bureau.

In the field of the unification of measures, the Bureau has had occasion to determine the relation between the metric units and certain national units, ancient or still legal. Examples are the Toise du Pérou and the rules of Borda; the toises of Bessel and No. 9 of the Prussian Geodetic Institute, the former having served as reference standard for all the geodetic operations in Central Europe at the middle of the nineteenth century; the double toise of Vienna; the double toise of Poulkovo; the yard and the pound of the British system.

*Thermometry.* Thermometry is the essential base of all metrology; it is impossible to conceive of any precise measurements that do not involve an accurate knowledge of the thermal conditions of the experiment. In view of the importance of temperature, one of the first tasks of the Bureau was therefore to study the improvements that might be applied to procedures used for its determination and the unification of the thermometric scale. This task was all the more indispensable because, toward the middle of the previous century, every phenomenon dependent on temperature was most often expressed on the scale peculiar to the thermometer of the experiments.

In the first place, the mercury thermometer really became a precision instrument when hard glass came into use for thermometers and after the studies by Guillaume had clarified the rules to be followed when using this type of thermometer. Correctly employed, the mercury thermometer permits the measurement of temperatures with a precision of a few thousandths of a degree in the interval from 0° to 100°C. The thermometers made by Tonnelot and Baudin between 1884 and 1913 have never been surpassed in quality of construction; they still serve as standards of the first order in many laboratories.

At the same time, the establishment of a unified temperature scale, to which the arbitrary readings of all the thermometric observations could be referred, was confided to P. Chappuis. His studies of gas thermometers (air, nitrogen, carbon dioxide, hydrogen) led to the adoption of the hydrogen thermometer as the normal temperature scale and the determination of corrections of the mercury thermometers in comparison with this scale.

Though limited until now to only slightly elevated temperatures, the thermometric studies of the Bureau have nevertheless contributed to the knowledge of the properties of toluene and other liquids as thermometric materials for measuring low temperatures. In 1897 P. Chappuis and J. Harker also compared platinum resistance thermometers with the hydrogen thermometer.

The measurements on the resistance thermometer had to be repeated at the Bureau as part of the plan to realize the *International Temperature Scale.* It must be remembered that this practical scale, which brings into actual being the absolute thermodynamic (Kelvin) scale, effectuates the closest possible agreement with the thermodynamic Celsius scale, as it is now known, by relying on a certain number of fixed points which serve as reference temperatures.

Although the resistance thermometer has now taken the place of the mercury thermometer in numerous experiments, the latter nonetheless remains a widely used instrument because of the ease with which it can be employed. Accordingly, studies of precision mercury thermometers are being continued at the Bureau on

thermometers with bulbs and stems of fused silica, in the hope of producing instruments that are free from the familar changes (secular change and depression after heating) of the "zero point." These displacements, which are not taken into account by many workers who are insufficiently informed, often lead to erroneous temperature measurements and are the chief cause of dissatisfaction with mercury thermometers.

*The Acceleration Due to Gravity.* The absolute value of the intensity of the gravitational force ($g$) is involved in the definition and absolute measurement of certain units. Therefore, an exact knowledge of the magnitude of this physical quantity, whose precise determination is a delicate procedure, is important.

Absolute determinations of this quantity have been made rather recently at Washington, Teddington, and Leningrad by the pendulum method. It was therefore of the highest interest that the Bureau likewise should participate in the determination of $g$, a measurement that moreover had been made at the Pavillon de Breteuil in 1888 by Defforges, using the pendulum method.

The new determination of $g$ undertaken by Volet at the Bureau replaces the classic pendulum method with a ballistic procedure, namely the fall of bodies, which is applied for the first time to a high-precision measurement. This venerable method, which can now be used with accuracy, thanks to modern techniques in the precise determination of very short time intervals, consists in taking moving pictures of a graduated rule in free fall and from them deducing its acceleration. The results of the first group of trials gave the following value:

$$g \text{ (Pavillon de Breteuil)} = 980.916 \text{ cm./sec.}^2$$

with a precision of several milligals.[10] Certain improvements, which deal chiefly with the production of flashes of light of the shortest duration, are now being applied to the initial setup and new measurements are planned.

This result, close to those obtained at Washington and Teddington, confirms the discrepancy observed with respect to the value found at Potsdam in about 1900—a value that was adopted internationally as a system of reference—which appears to be about 20 milligals too high.

The results already obtained, to which there has just been added the determination being made at Ottawa, which likewise employs the principle of the Volet method, leaves no doubt that the Potsdam value will have to be revised and a new point of departure set up for the relative determinations of $g$.

*Volume of the Kilogram of Water.* It will be recalled that the founders of the metric system based the unit of mass on the unit of length through that of volume. Their intention was to define the unit of mass by the relation: 1 kg. = the mass of 1 cubic decimeter of water at 4° C. Did the Kilogramme des Archives actually conform to this definition? Some doubts being raised on this point, the Bureau decided to undertake the determination of the volume of the kilogram of water. These delicate measurements were made several times between 1895 and 1907, using the general method of determining, by linear measurements, the volume of a body with a regular form, and then determining, by hydrostatic weighings, the loss in weight of the body when submerged in water. The linear dimensions of the bodies employed (bronze or brass cylinders, cubes of crown glass and quartz) were determined either by means of a caliper comparator (cylinders) or by interferential methods (cubes). The final result of this important study, with which is associated the names of Ch. Ed. Guillaume, P. Chappuis, Ch. Fabry, Macé de Lépinay, H. Busson and J. R. Benoît, led to the value 1.000028 cubic decimeters for the volume of a kilogram of pure air-free water at its maximum density (4° C.) and under normal atmospheric pressure.

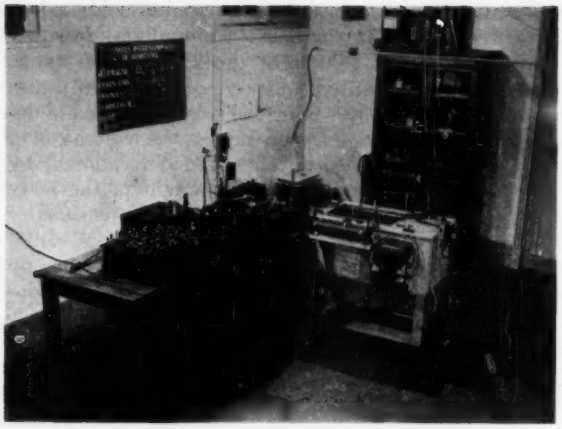
The *liter*, which is equal to the volume occupied by the mass of a kilogram of water, therefore exceeds the volume of the cubic decimeter by 28 millionths, or 1 liter = 1.000028 cubic decimeters. This deviation represents the difference between the mass of the International Kilogram and that of the cubic decimeter of water, the original definition of the kilogram, and shows with what precision—aided perhaps by chance—Lefevre-Gineau and Fabbroni constructed the kilogram a century and a half ago.

This distinction between the *cubic decimeter* (unit of volume related to measures of length) and the *liter* (unit of capacity related to measures of mass), a distinction limited to measurements of high precision, is somewhat of a black mark against the impeccability of the metric system. Consequently, it might be desirable to have an international decision with the purpose of doing away with this duality, which the founders of the system certainly never envisaged.

*Interferometry.* As soon as methods were perfected for measuring the wave lengths of luminous radiations—those lengths which Fizeau declared constitute a *natural* micrometer of the greatest possible perfection—there was immediate appreciation of the possibilities offered by the phenomena of light interference for checking the permanence of the unit of length, as materialized in the platinum-iridium prototype, and for measuring the end standards with increased precision.

The production of a natural *témoin* of the unit of length and the assignment to spectroscopy of its definitive scale as a function of the metric unit, were the objectives of the studies made at the Pavillon de Breteuil in 1892–93 by A. A. Michelson and J. R. Benoît. They established for the first time the relation of the wave length of the lines of the cadmium spectrum to the international meter. In 1906 J. R. Benoît, Ch. Fabry, and A. Perot repeated these measurements by new procedures, which permitted the observation of fringes of superposition (Fabry-Perot standards) and confirmed the results of Michelson and Benoît obtained with the Michelson interferometer and standards.

[10] The *gal* (abbreviation of Galileo, the discoverer of the laws of the fall of bodies) is the cgs unit of acceleration; it corresponds to an acceleration of 1 cm./sec.$^2$



**One of the Laboratory Rooms of the International Bureau Showing Apparatus for Comparing National Standards of Electrical Resistance**

As the result of these determinations, the wave length of one of the cadmium lines—$\lambda = 0.64384696\ \mu$ (the red line)— was finally selected to play the double role of *témoin* of the meter and fundamental standard for light waves.

Among the principal interferential researches carried out at the Bureau were the determination (with the Fizeau apparatus) of the coefficient of expansion of the platinum-iridium alloys of the prototype meters, and of various materials (pure platinum and iridium, bronzes, brasses, and various steels, gold, quartz, beryl, Iceland spar) and the index of air; the measurement with the Michelson interferometer of the end standards constructed of crystalline quartz, which constitute the third *témoin* of the metric unit; the study of the best monochromatic spectral lines with respect to their use in metrology; the perfection of the interference methods and the construction of an interferometer for the measurement of industrial gages of the Johansson type, etc. All of these studies, made by J. R. Benoît and A. Pérard, are now being continued by J. Terrien.

At present, the Bureau is particularly interested in the lines of single isotopes (nuclides); on one hand, the lines of mercury 198, a new element produced for the first time in the U. S. A. by the transmutation of gold bombarded with neutrons from an atomic pile; on the other hand, those of the two nuclides, krypton 84 and 86, produced in Germany by thermodiffusion. These new light sources, which give very fine lines that are perfectly monochromatic, are observable at large path differences and, from the metrological point of view, they doubtless are superior to the red line of cadmium. They are now the object of intense study at the National Bureau of Standards (U. S. A.), at the National Physical Laboratory (Great Britain), at the Physikalisch-Technische Bundesanstalt (Germany), and at the International Bureau.[11]

[11] Mercury 202, recently isolated in the U. S. A. by electromagnetic separation, has also been suggested as a source of perfectly monochromatic light.

These recent studies have again brought to the fore the question of replacing the platinum-iridium bar (material standard) by a wave length as a *natural* standard of length. In 1948, the ninth General Conference of Weights and Measures considered a proposition along these lines, looking toward the abandonment of the present definition of the meter in favor of a suitably chosen wave length.

The idea of taking a wave length as standard of length is quite old, since it was first advanced in 1827. However it was fortunate that a too hasty decision was not made. Studies of spectral lines have progressively revealed the influence of various factors on the wave length of these lines. It was these latter reasons that caused the ninth General Conference not to make an immediate decision regarding the proposed change, and to wait until additional new studies of mercury 198 and krypton 84 and 86 confirm the results of the first experiments.

*Electric and Photometric Units.* The seventh (1927) and the eighth (1933) General Conferences of Weights and Measures directed the Bureau to establish and preserve electrical and photometric units, and to compare national and other precision standards with these standards, and also to make studies leading to the improvements to be applied to standards, to measuring instruments, and to methods of observation.

This new field of activity of the Bureau however presents a somewhat different situation than that of units of length and mass. The value of all the electrical quantities (which derive from the cgs system) is deduced from two of them, the ohm and the ampere, determined in absolute units, a determination which involves only the measurement of fundamental mechanical quantities: length, mass, time. For photometric quantities, the present primary standard is a black body functioning at 2042°K. (solidification point of platinum).

The determination of the ohm and the ampere in absolute units and the construction of a black body required many detailed preliminary studies and protracted and delicate measurements, which could only be made at more or less scattered periods in specially equipped laboratories. After these determinations were once accomplished in a national laboratory it became the function of material secondary standards to preserve the value obtained for each unit: standard ohm of manganine wire for the unit of resistance; Weston cell for the unit of electromotive force; incandescent lamps for units of luminous intensity and luminous flux at different color temperatures.

Up to the present the Bureau has not been given the task of measuring the absolute ohm and ampere nor of preparing the standard black body. Strictly speaking, there are no international primary electrical or photometric standards to which the units of each country may be related, as is the case with the meter and kilogram.

Accordingly, the international comparisons to be made by the Bureau will deal with the material electrical and photometric standards. To this end, six

national laboratories[12] have been invited to send to the Bureau the secondary standards which represent the unit as it has been constructed in each of these laboratories.

Since the installation, in the new laboratories constructed for this purpose in 1930, of the necessary measuring instruments—bridge potentiometer, double Thomson bridge, photometric bench, Ulbricht sphere, etc.—these comparisons have been made periodically. The results have made it possible to assign to the national standards a value in terms of a *mean international unit.* All of the electrical and photometric standards preserved at the Bureau, restandardized in the "mean unit" at each comparison, now constitute international prototypes of the ohm, the volt, the candela, and the lumen. Just as the Bureau has been made responsible for the units of length and mass, it thus assures, though by different means, the world-wide unification of the units of electricity and light.

Although these international comparisons, together with the checks of standards requested by national and private laboratories, obviously make up the bulk of work of these two sections of the Bureau, research activities are none the less also pursued. In the field of photometry, for instance, J. Terrien, head of this section, has made many studies which among other things have resulted in raising the quality of the standard lamps, and improving the methods and measuring equipment and increasing the precision of the observations, the final goal of all the efforts of metrologists.

*The Three Advisory Committees.* When the electrical and photometric units were assigned to the Bureau, the members of the International Committee felt that it would be necessary to create for itself advisory committees on electricity and photometry composed of specialists in these fields from all over the world. It is the duty of these committees to coordinate all the studies on electrical and photometric matters and to suggest, in the form of recommendations to the International Committee and the General Conference, modifications of the definitions and values of the existing units. Later (1937) an Advisory Committee on Thermometry has been similarly instituted and its jurisdiction has been extended to calorimetry.

The latest investigations of these three committees were presented to the 1948 General Conference. The principal decisions and resolutions adopted were:

(1) *Electricity:* (*a*) Substitution, after January 1, 1948, of the system of *absolute units* for the so-called "international units," that had been defined by the conference of 1908; (*b*) Fixing of the conversion factors from the old to the new units:

| | |
|---|---|
| 1 ohm (international mean) | = 1.00049 ohms (absolute) |
| 1 ampere (international mean) | = 0.99985 ampere (absolute) |
| 1 volt (international mean) | = 1.00034 volts (absolute) |

(2) *Photometry:* Adoption of the new unit of light intensity, the candela, defined from the luminescence of the integral radiator (black body) at the solidification temperature of platinum.

(3) *Thermometry:* (*a*) Publication and approval of the text of the "International Scale of Temperature," 1948. (*b*) Use of the word *Celsius* (° C.) to designate the degree of temperature, replacing the terms "centigrade" and "centesimal." (*c*) Resolution relative to substituting the melting point of ice by the triple point of water ($t = +0.0100°$ C.) as thermometric reference point of the Celsius thermodynamic scale and the adoption of an absolute thermodynamic scale related to only a single fundamental fixed point (triple point of pure water). (*d*) Use of the *joule* as the unit quantity of heat, replacing the "calorie."

In addition to all these researches and metrological studies, the Bureau is often asked to give advice on matters relating to measures and their organization. Several governments have consulted the Bureau regarding the revision of laws and the organization of their Departments of Weights and Measures.

Recently, the International Committee has also been placed in charge of an official inquiry concerning scientific, technical, and pedagogic circles, with the view of adopting, for international relations, a practical international system of units. With this objective, a plan of the units, meter-kilogram-second-ampere (Giorgi system) has been taken as the basis of discussion. The results of this inquiry are to be submitted to the next General Conference.

## CONCLUSION

Such, in brief, is the history of the origins of the metric system of weights and measures and the work

**Photometry Laboratory of the International Bureau.** ***Right:*** **Photometric Bench and Integrating Sphere for Comparing National Standards of Luminous Intensity and Flux.** ***Left:*** **Rheostats for Regulating the Electrical Supply to Standard Lamps**

[12] Physikalisch-Technische Bundesanstalt and Deutsches Amt für Mass und Gewicht (Germany); National Bureau of Standards (U. S. A.); Conservatoire National des Arts et Métiers and Laboratoire Central des Industries Electriques (France); National Physical Laboratory (Great Britain); Electrotechnical Laboratory (Japan); Institute of Metrology (U. S. S. R.).

accomplished by the International Bureau of Weights and Measures during the 77 years of its existence.

From the plan of the reform of measures laid down by Talleyrand in 1790 there has grown a quasi-universal system of measures, whose merits of simplicity and coherence have been recognized also by the two principal nonmetric countries, England and the United States of America, countries which themselves played an important role in the history of its foundation.

If the metric system, despite its continuous extension during a century, does not yet cover the entire globe, it nevertheless appears certain that its universality will eventually be completed. The report drawn up in 1951 by the "Committee on Weights and Measures Legislation" and submitted to the English Parliament justifies every hope in this sense. In large part, the United States will dictate the decision to be made: to give up the "Imperial System" and compel the adoption of the metric system, or to continue the coexistence of the two systems with all the attending inconveniences.

As for the International Bureau, it is not, as some may think, merely the place where the standard meter and kilogram are preserved; rather it is an international center of standardization, housing a metrological laboratory. Although many solidly established international organizations have not survived the upheavals of two World Wars, the Bureau has been able, despite some temporary difficulties, not only to continue its work but even to accept more assignments and thus pursue the mission confided to it in a disinterested scientific spirit and in close communion with the principal national metrological laboratories.

Looking forward to the years ahead, it may perhaps be asked whether the revolution that is shaping up in the development of fundamental standards of length and mass—the "atomic" standards, as they already are called—will not decrease the prestige of the International Bureau, perhaps endangering its very existence. However, it seems certain that whatever may be the standards of the future, the important part which the Bureau has filled in the global unification of the units of measure and in the improvement of metrological science will guarantee its continued existence.

It was this confidence in the future of the International Bureau of Weights and Measures that motivated the signatory countries of the Convention du Mètre to adopt unanimously, at the 1948 General Conference of Weights and Measures, a resolution designed to develop the future activity of one of the oldest international institutions.

# INORGANIC PAPER CHROMATOGRAPHY

## *II. Separation of Groups III, IV, and V*

**JOHN G. SURAK, NORMAN LEFFLER, and ROBERT MARTINOVICH**

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In view of its ever increasing importance chromatographic analysis is being introduced to a greater extent to students of qualitative analysis as a supplement to the conventional method of analysis for the cations (*1, 2, 3, 4, 5, 6*). In the preceding papers (*1, 4*), cations of Groups I, IIa, and IIb were separated and identified by means of paper chromatography. This paper concerns itself with the separation and identification of the cations of Groups IIIa, IIIb, IV, and V.

The equipment used was of the type previously reported (*4*). The only variation in the technique was that the ions were applied on the filter paper by means of a camel's hair brush. It was found that more uniform bands were obtained by this method than by the capillary pipet method.

In the case of Groups I and II, a single chromogenic reagent sufficed to identify the cations, namely, 0.2 per cent $K_2CrO_4$ for the Ag group and $H_2S$ for the Cu-Sn group. However, in the case of Groups III and IV, individual chromogenic reagents will have to be used for the identification of the respective cations.

In the preparation of the solutions, the chlorides of the metals were used. For Group III, the solutions were made 0.2 per cent (W/V); those of group IV were made 0.2 *N*. The solvents were made up on a percentage basis (V/V). The pH was determined by means of a pH meter, although Hydrion paper may be used as in the previous paper.

The following technique is utilized for the determination of the bands: After the development of the chromatogram and subsequent drying for the removal of the solvent, a camel's hair brush dipped in the identifying reagent is touched along the edge of the paper in order to reveal the location of the bands. When the position is located, that area is then brushed with the reagent to bring out the entire band.

The ratio of the movement of the solute to that of the solvent is defined as the Rf factor. Although this is consistent for a given set of variables, such as temperature, pH, time, solvent, complexing agents, etc., it loses its usefulness as a means of identification when any of the previously mentioned variables are changed. The conditions must always be the same for any reproducibility of Rf values.

**Group IIIa (Aluminum Group)**

TYPE OF PAPER: Whatman's 3-mm.
TIME OF DEVELOPMENT: 24 hours
DEVELOPING SOLVENT
70% Tertiary butyl alcohol
30% Water
pH adjusted to 2–3 with HCl

| | Rf's @ pH 2 | Rf's @ pH 3 |
|---|---|---|
| Al | 0.232 | 0.382 |
| Zn | 0.416 | 0.540 |

| *Cation* | *Identifying Reagent* | *Color* |
|---|---|---|
| Al | Aurin tricarboxylic acid | Light red |
| Zn | Dithizone in $CCl_4$ | Pink |

**Group IIIb (Iron Group)**

TYPE OF PAPER: Whatman's 3-mm.
DEVELOPING SOLVENT
87% Acetone
8% HCl (6 *N*)
5% Water
TIME OF DEVELOPMENT: 3 hours

| | Rf's |
|---|---|
| Fe | 1.000 |
| Co | 0.326 |
| Mn | 0.113 |
| Ni | 0.048 |

DEVELOPING SOLVENT (*7*)
97% Acetone
3% HCl (6 *N*)
TIME OF DEVELOPMENT: 23 hours

| | Rf's |
|---|---|
| Fe | 1.000 |
| Co | 0.904 |
| Mn | 0.820 |
| Ni | 0.021 |

| *Cation* | *Identifying Reagent* | *Color* |
|---|---|---|
| Fe | Potassium ferrocyanide | Blue |
| Fe | 0.2% Nitroso-β-naphthol | Grayish-black |
| Co | 0.2% Nitroso-β-naphthol | Reddish-brown |
| Mn | 0.05% Benzidine base (standard method) | Blue |
| Ni | 1% Alc. Dimethylglyoxine | Red-pink |

**Group IV (Alkaline Earth Group)**

TYPE OF PAPER: Whatman's 3-mm.
TIME OF DEVELOPMENT: 6–7 hours

| DEVELOPING SOLVENT<br>40% Isopropyl alcohol<br>40% Water<br>20% HCl (6 *N*) | | DEVELOPING SOLVENT<br>40% Isopropyl alcohol<br>30% Water<br>30% HCl (6 *N*) | |
|---|---|---|---|
| | Rf's | | Rf's |
| Ca | 0.63 | Ca | 0.93 |
| Sr | 0.55 | Sr | 0.61 |
| Ba | 0.40 | Ba | 0.48 |

| *Cation* | *Identifying Reagent* | *Color* |
|---|---|---|
| Ca | 2% Alc. alizarin | Violet |
| Sr | 0.2% Potassium rhodizinate | Yellow-orange |
| Ba | 0.2% Potassium rhodizinate | Red |

**Group V (Alkali Metals Group)**

Group V has been separated by several investigators (*7*, *8*, *10*). S. Chakrabarti and D. P. Burma (*10*) suggest the following:

TYPE OF PAPER: Whatman's No. 1
Neutral solution of their chlorides (1%)

| DEVELOPING SOLVENT<br>Methyl Alcohol | | DEVELOPING SOLVENT<br>Ethyl Alcohol-Water (7:3) | |
|---|---|---|---|
| | Rf's | | Rf's |
| K | 0.22 | K | 0.41 |
| Na | 0.44 | Na | 0.52 |
| Li | 0.72 | Li | 0.65 |

The positions of the cations are found by spraying with a mixed solution of silver nitrate and fluorescein (*7*) and then drying the strip. Characteristic dark bands reveal their presence.

Additional work needs to be done on certain of the cations, especially in the field of identifying reagents. In the case of benzidine base for manganese, the color fades in about 5 minutes; also, the spot with the indicator must be made alkaline to bring out the color. V. Hovorka and Z. Holybecker (*9*) suggest the use of 2,3-butanedione oxime thiosemicarbazone as a sensitive microchemical test for manganese. A red-violet color indicates the presence of manganese when made ammoniacal. The test for calcium must be conducted in the absence of ammonia fumes as the latter will also give a violet color with alizarin.

While the scheme of analysis presented in these two papers is based on the conventional qualitative analytical groups, some investigators (*11*) have suggested a classification of the cations into qualitative chromatographic groups based on the separation of these ions by means of specified selective solvents.

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# THE CHEMICAL PROPERTIES OF THE METHYL GROUP[1]

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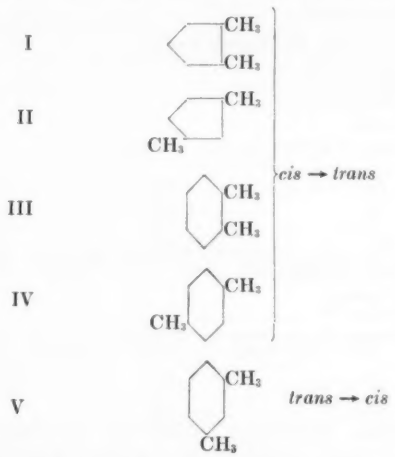
I HAVE chosen to follow through a particular small and simple problem which crops up again and again in the study of organic chemistry, namely, the question of what the methyl group is like, and why it does the things it does. The work is not chiefly my own but that of many workers throughout the world and over a number of years. I have counted roughly 17 different methods of approach which have been used in the attempt to shed light on the methyl group. The methyl group is certainly one of the simplest of organic groups, and it is not a group of extreme character of any sort. One might well hope to be able to understand the methyl group fairly early in the course of studying the structures of organic compounds and the mechanisms of organic reactions.

## CIS AND TRANS FORMS

Let us consider a Fisher-Hirschfelder model of two methyl groups combined to give ethane with free rotation about the bond joining them. First, let me recall some of the research that went into the construction of models of this type. These models do not attempt to show the location of atomic centers, but undertake to show a sort of interference radius around each atom. The determination of that interference radius has been done by the combined results of a number of physical methods, prominent among which is study of the viscosity of diatomic gases, the zero point extrapolated volumes of liquids, and the distance between atoms in crystals. The radii which are shown here are derived from the distances to which nonbonded atoms will approach before they begin repelling each other with sufficient force to start rebounding in an average collision at room temperature. It looks from this model as if the one methyl group in ethane were free to rotate around the carbon-carbon bond joining it to the other methyl group, and yet we know from some other physical methods that this is the case only to a limited extent. By comparing the entropy of ethane calculated from spectroscopic data with that determined by heat-capacity measurements down close to absolute zero, it can be shown that there is a restriction, an energy barrier that the methyl group has to get over three times in every rotation, corresponding to the fact that the energy content of the "opposed" constellation in ethane is about 2800 cal./mol higher than that of the completely staggered form. This gives rise to a whole group of properties in small or medium-sized ring compounds which are just in the process of becoming well understood.

The formulas below show the equilibrium relationships, or, at any rate, the direction of greatest stability in the *cis*-and *trans*-dimethylcyclopentanes and dimethylcyclohexanes. *Cis*-1,2-dimethylcyclopentane (I) and *cis*-1,3-dimethylcylopentane (II) are unstable with respect to the *trans* isomers; this is what might be expected if the adjacent non-bonded hydrogens repel one another, and would prefer to be on opposite sides of the plane of the ring rather than on the same side.




*Cis*-1,2-dimethylcyclohexane (III) is unstable thermodynamically with respect to *trans*. (This does not mean that the isomers interconvert readily, but it is possible to establish the position of equilibrium by determining the relative free energies.) All of these *cis* isomers are found to be unstable with respect to the *trans*, but the 1,3-dimethylcyclohexanes (V) show the opposite behavior. The *trans* isomer is unstable with respect to the *cis*. This result, which was unexpected prior to appreciation of the energy barriers which are caused by hydrogen-hydrogen interactions, is now well understood and has been the subject of several papers by Pitzer, Rossini, and others (*1*).

Figure 1 shows two kinds of models of the so-called "chair" form of cyclohexane. This "chair" form of cyclohexane involves a relationship of the hydrogens on adjacent positions which is like that of the hydrogens in the staggered phases of the rotation of ethane, and therefore since each hydrogen is as far from its neighbors as it can get, this configuration represents a substantially more stable form of cyclohexane than

[1] The Seventh Annual Harrison Howe Lecture, presented under the sponsorship of the Rochester Section of the American Chemical Society on November 16, 1951.

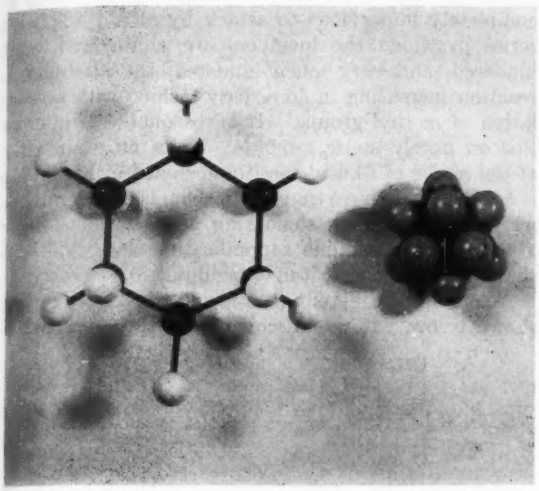


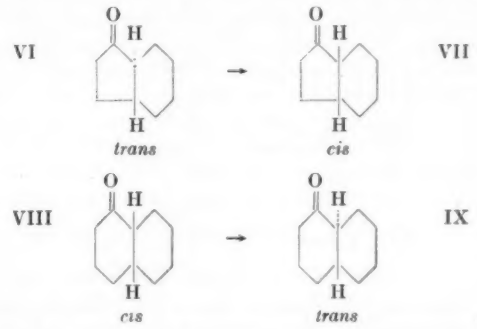
Figure 1

does the "boat" form. The latter has some hydrogens in the opposed position and particularly at the bow and stern of the boat where hydrogens in the *para* position come too close together. It is now well recognized that the hydrogens in the chair form, the most stable form of cyclohexane, are arranged in three kinds of positions. There is a set of *trans* hydrogens around the periphery known as equatorial hydrogens, there is a set of three hydrogens which are *cis* to one another and which are seen from this side, and the three missing hydrogens (we see only 9 of the 12) are in a corresponding pattern on the opposite faces of the other three carbon atoms. As far as the hydrogens are concerned, it makes very little difference whether a hydrogen atom is in a polar position or in an equatorial position, because it comes about equally near to its neighbors in either position. But the relationship of the three polar hydrogens is such that if they were larger atoms instead of hydrogens, they would begin exhibiting some repulsion across the *meta* positions.

Figure 2 shows models of the 1,2- and the 1,3-dimethylcyclohexanes which help to show why it is that in one case the *cis* form is the more stable and in the other the *trans*. It can be readily seen from one of these models that if the two methyl groups in the 1,2-compound arrange themselves in equatorial positions, they are *trans* to each other, and are not interfering with each other very badly. In the *cis*-1,2-dimethylcyclohexane, however, if we put one methyl group in an equatorial position as it is seen to be here, the other methyl group has to go into a polar position. Notice how close the hydrogen comes to the existing hydrogens in the polar positions. There is a tight enough fit here to prevent free rotation of the methyl group. It is not surprising that the *cis* form of 1,2-dimethylcyclohexane is unstable relative to the *trans* form which does not have these close interactions. Now when we go to the 1,3-dimethylcyclohexane, the situation is exactly reversed. It is in the *cis* form that the two methyl groups both occupy the relatively strain-free equatorial positions, whereas in the *trans* form, if one methyl is equatorial the other methyl has to be polar, and again it looks unfavorable to make the methyl group polar on the basis of these formulas.

These facts about the peculiar position of the 1,3-dimethylcyclohexane have been explained entirely on a steric basis, regarding the methyl group only as something that occupies space. Many of the things the methyl group does arise from its character as a thing that occupies space, and are independent of any chemical character.

The fact that a staggered chair arrangement of the cyclohexane ring is preferred was of course known by organic chemists before the calculations of entropy and energy barriers had been put on a quantitative basis. Another observation which points to a considerable stability of the staggered form of the cyclohexane ring is due to Hückel (*2*). This is the fact that whereas, in hydrindanone (VI), in which a five-membered ring is




fused with a six-membered ring, the compound with *trans*-fusion under enolizing conditions goes over into the *cis* form (VII), yet just the opposite happens when

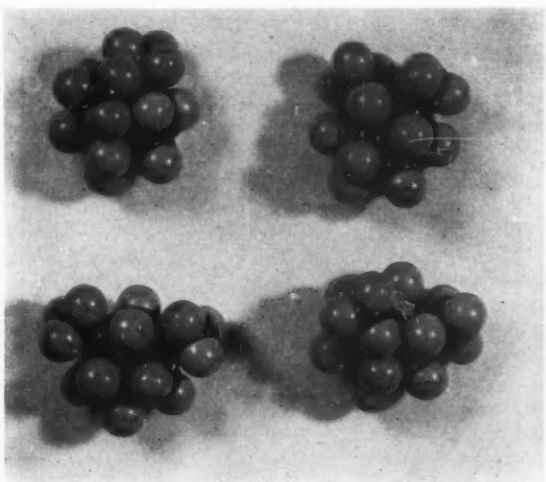


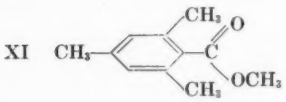
Figure 2

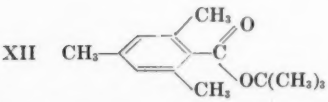
the two six-membered rings are fused. There the *cis* form goes over into the *trans*. A model of the *trans* form of the decalone IX can be made very nicely with staggered "chair form" rings all around. A model of the *cis* form VIII requires that one ring assume a position different in some respects from the completely staggered. The fact that the energy relationships favor this is direct evidence of an organic sort in favor of the staggered configuration of the cyclohexane ring.

## SPACE-FILLING EFFECT

There are a number of other properties of the methyl group that look as if they should be explicable on strictly steric grounds, but they are seldom completely straightforward. A classical example of the behavior of the methyl group as a space-filling group, a group that hinders chemical reaction by shielding the center, is the behavior of esters of mesitoic acid.

The alkaline hydrolysis of esters is one of the most studied reactions in organic chemistry, and it goes well at a measurable rate with methyl benzoate (X). It




goes, however, very poorly with a di-ortho-substituted methyl benzoate such as XI, with methyl groups retarding addition to the carboxyl. If we substitute completely with methyl groups not only in the ortho positions, but also on the alcohol group of the ester X, we have *t*-butyl mesitoate (XII). This compound is completely impervious to attack by alkali. This is a series in which the members are unhindered, much hindered, and very much hindered, the hindrance to reaction increasing in an orderly fashion with accumulation of methyl groups. It is reasonable to interpret this on purely steric grounds. From an examination of the model of *t*-butyl mesitoate shown in Figure 3, it is not hard to believe that any mechanism of hydrolysis which requires that something add to the carbonyl group, as this alkaline saponification does, will be so sharply hindered that it may be impossible to carry out.

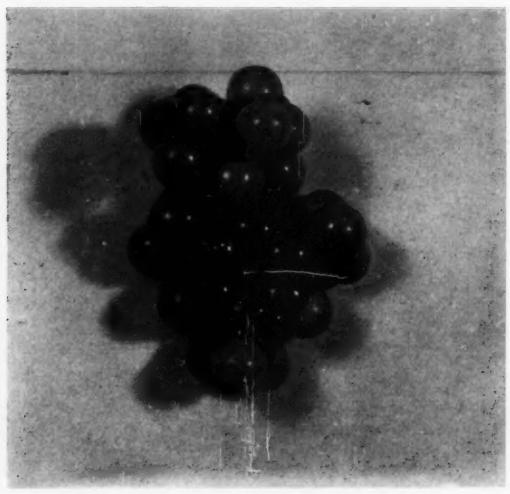
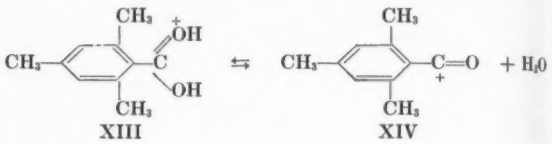


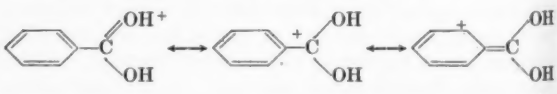
Figure 3

A somewhat different reaction in the same family is shown below. It was discovered by Hammett in con-

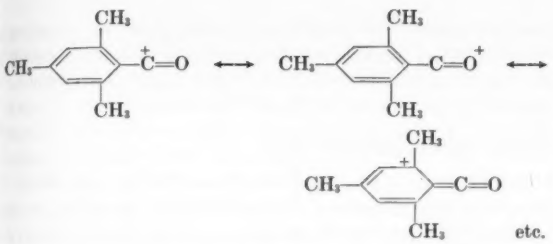



nection with his cryoscopic studies (*3*) that if a highly hindered methyl benzoate is dissolved in concentrated sulfuric acid and poured into cold water, an immediate hydrolysis takes place and the acid is produced, provided that the aromatic group is highly hindered by methyl groups. Plain methyl benzoate, under the same conditions, yields the ester back. The same thing works in reverse. A solution of mesitoic acid in 100 per cent sulfuric acid poured into absolute methanol yields the ester immediately—a corollary of this work followed up by Newman (*4*). Benzoic acid, so treated, yields only benzoic acid again; thus here we have the same compound being abnormally inert to one mode of esterification and abnormally reactive to another. The explanation for this is again based primarily on stereochemical considerations, but they require also a consideration of the details of the mechanism—what happens when a substance of this type is dissolved in sulfuric acid. When methyl benzoate is dissolved in sulfuric acid a proton occupies the oxygen, and we get the ester with $H^+$ on it and nothing else. When an ester of mesitoic acid or mesitoic acid itself is dissolved in concentrated sulfuric acid this may be the first step, but something else happens. Methanol or water (as the case may be, whether we are using the ester or the acid) is split out, combined with sulfuric acid, and what is left is an ion ending in a $CO^+$, an acyl cation in solution. Why is the acyl cation formed in the hindered and not in the unhindered case?

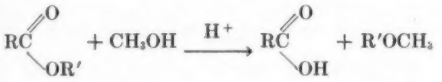
The resonance which stabilizes the ion




requires coplanarity of the system, which is prohibited in the hindered structure, XIII, and this difference is enough to shift the equilibrium significantly toward the acyl cation XIV, which is unaffected by the *ortho* methyl groups.




Let us take one more case of reactions in the mesitoic acid series. The equation illustrates the meth-




X: no reaction XI: no reaction XII: rapid reaction

anolysis of an ester, which is not the usual attack of a hydroxylic compound on the carbonyl group of an ester but an attack on the alkyl-to-oxygen bond; this is a possible mode of reaction of an ester which is rarely observed. The ester reacts with the methanol in such a way that the R′ on the alkyl group of the ester turns up as a methyl ether and the acid is liberated in the free state.

This reaction is not shown by methyl benzoate, nor by methyl mesitoate, but it is shown by *t*-butyl mesitoate (*5*), the compound which is so hindered toward alkali that it does not saponify at all. This cannot be accounted for by either of the previous mechanisms, but it still proved to be a kind of effect of the methyl group which needs to be considered. It is believed that this is a case not only of the shutting off of other modes of reaction but the appearance of a polar property of the methyl group which greatly enhances the ability of the alkyl group to carry a positive charge. This is currently interpreted as being an ionization process producing the mesitoate anion and the *t*-butyl cation reacting with the solvent. Here we have a reaction in which the methyl group is not functioning solely as a space-filling group, but is helping to accommodate the positive charge on the carbonium ion.

Along these lines I might quote some rather striking rates of reaction in simpler compounds which presumably proceed by this same mechanism. Table 1 shows some rates which were measured by Dr. Marguerite Swain at Radcliffe a few years ago. These chlorides are dissolved in an aqueous solvent, but because some of them react very rapidly we could not use pure water or even 50 per cent water-acetone, but a solvent containing 90 per cent acetone and 10 per cent water in which ordinary tertiary chlorides react extremely slowly. The table reports the rate constants of components of the solutions relative to *t*-butyl chloride taken as unity. The table lists the alcohol because we know the structure of the starting alcohol. We do not in all cases know the structure of the chloride which was measured; we know only its rate. This is because of the extreme instability of the chlorides, a problem on which we are still working. It is very hard to see how the polar character of the methyl group can account for the enormous increase in rate, shown in the table, accompanying the insertion of methyl groups in the last remaining positions. A model of tri-*t*-butylcarbinol built up with Fisher-Hirschfelder atoms shows that there is not a single space left where anything more could be put into the sphere immediately surrounding the central carbon. Every methyl group is fitted very closely to its neighbors, and no methyl group can rotate with respect to its neighbors, so that we suspect again steric considerations.

**TABLE 1**
**Relative Hydrolysis Rates of Chlorides (90 per cent Acetone)**

| *Alcohol source* | *Relative rate* | *Per cent present in chloride measured* |
|---|---|---|
| $(CH_3)_3COH$ | 1.0 | 100 |
| $[(CH_3)_2CH]_3COH$ | 5.5 | 93 |
| | 250 | 7 |
| $[(CH_3)_2CH]_2COH$ | | |
| $(CH_3)_3C$ | 1,300 | |
| $[(CH_3)_3C]_2COH$ | 40,000 | 45 |
| | 3,000 | 22 |
| $(CH_3)_2CH$ | 210 | 21 |
| | 2,600 | 63 |
| $[(CH_3)_3C]_3COH$ | 130 | 25 |

## NATURE OF STERIC EFFECT

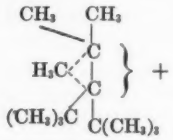
There have been two suggestions made as to the nature of the steric effect. The suggestion of Herbert Brown (*6*), based on *B* strain, is shown schematically below. Brown points out that the tetrahedral angle between the groups connected to the central carbon in the

starting chloride is 109° 28′, which implies much crowding with any really branched group. But if it ionizes, and if that is the mechanism of the hydrolysis or of the elimination reaction the resulting structure is coplanar with bond angles of 120°. This is a marked release of strain. The amount of release of strain is proportional to the tightness of fit, and if the central atom is becoming greatly crowded, further substitution of methyl groups will greatly increase the release of strain which will accompany ionization.

We are not convinced that this is the entire story in the reactions of highly branched compounds for the following reason. The picture suggests that this cation should be particularly stable, since any further reaction that it might undergo would entail further crowding due to the closeness of the methyl groups. The fact is that these compounds apparently always react

with molecular rearrangement to highly branched olefins. The tri-*t*-butylcarbinyl chloride cannot give an olefin without molecular rearrangement, but when it reacts in 90 per cent acetone it gives entirely an olefin; therefore it reacts entirely with molecular rearrangement, and the olefins which might be formed all look more crowded than this carbonium ion. So we wonder if, indeed, a carbonium ion is formed, and if so, what makes it go back to something more constricted.

An alternative explanation of the effect of high branching on the enhanced reactivity of these chlorides is based on the work of Winstein, Cram, and their coworkers (*7*), who have shown that in some of the well-known molecular rearrangements there is an intermediate ion formed of a curious type with a bridge, in which a saturated group is simultaneously partly bonded to two adjacent atoms. We suggest that the peculiar thing that has happened under conditions of



very close crowding in the highly branched compounds is that the methyl groups are all pushed so close together that they invade what would normally be one another's sphere of privacy based on the interference radii which are shown in the Fisher-Hirschfelder models. They are so close that they are within incipient bond-forming distance of one another. In certain bicyclic compounds such as compounds of the camphane series, bicyclo-(2,2,1)-heptane series and in cholesterol, it has been shown that the ability of a group to start forming structures of this kind is associated with a greatly increased speed of ionization (*8*). Thus the steric acceleration of ionization in the highly branched halides may arise not simply from atoms pushing one another apart, but from their jumping at one another on account of being crowded so close that they break one another's defenses down, and this makes for a greater speed of actual chemical reaction.

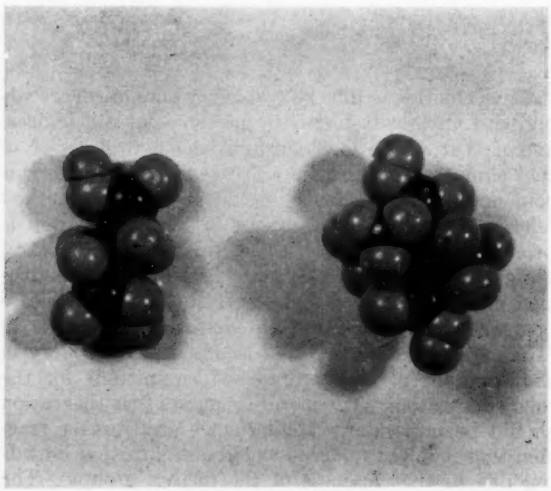


Figure 4. Succinic Acid (left); Tetramethylsuccinic Acid (right)

## SPACE-EXCLUDING EFFECT

Another mysterious effect of methyl groups which has been the subject of a good deal of speculation is typified by the case of the two ionization constants of tetramethylsuccinic acid. The first ionization constant of succinic acid is much greater than the second, and the ratio of those two constants is 19, as shown in Table 2.

**TABLE 2**
**Methyl Groups and Ionization Constants**

| *Acid* | $K' \times 10^4$ | $K'' \times 10^7$ | $K'/K''$ |
|---|---|---|---|
| $CH_2$—COOH<br>$CH_2$—COOH | 0.64 | 33.3 | 19.2 |
| $(CH_3)_2C$—COOH<br>$(CH_3)_2C$—COOH | 3.19 | 0.52 | 6135 |

The mere insertion of four methyl groups on the main chain increases the acid strength of the first carboxyl by more than one-hundredfold and decreases the acid strength of the second carboxyl by almost one-hundred fold, so that the ratio between the first and second acid strengths has gone up from 19 to over 6000 just by putting in the four methyl groups. Since the first ionization constant has gone up and the second constant has gone down, this cannot be blamed on either an electron-releasing or an electron-attracting property of the methyl group. Again, it looks as if the methyl group is a versatile structure which is facing both ways, and perhaps this is a space-occupancy effect. An ingenious attempt to account for this made by Ingold (*9*)—an attempt which, however, was not successful—was based on the postulate that the actual distance between these two carboxyls changed. According to electrostatic theory, if the two carboxyls should come closer together the charge which is left after the dissociation of the first one would so influence the second as to lower its acid strength, and on the other hand the dipole effect of the undissociated carboxyl on the first ionization constant would likewise be enhanced, and that would be opposite in sign. But from the distance measurements that have been made there is no basis for the idea that these two carboxyls are particularly different in their separation when there are four methyl groups present and when there are not. The answer to this particular question was provided by Kirkwood and Westheimer (*10*) and the basis of the reasoning may be seen from Figure 4. The model of succinic acid is arranged in the staggered form which is believed to be relatively stable. The distance between the carboxyls in the two molecules is the same, but there is a great filling out of space between those with the methyl groups. The dielectric constant of methyl groups must be about the same as the dielectric constant of

kerosene or any paraffinic liquid. It is very low indeed. These measurements are made in water, so that in the tetramethyl compound some water which comes in close to the succinic acid molecule is replaced as if by some kerosene—actually by some methyl groups with very low dielectric constant. Kirkwood and Westheimer succeeded in calculating how the size and shape of a cavity of low dielectric constant in a medium of high dielectric constant should affect the electrostatic force between the two ends. If we deal with a thin ellipsoid and have water outside the cavity and material of low dielectric constant inside, the force between two charges or two dipoles is very much less than it is in a sphere or a very broad ellipsoid, in which the volume of low dielectric contant has been increased.

Now certainly this, too, is a steric effect of the methyl group, an effect occurring because the methyl group occupies space. However, the methyl group is not blocking access to a reaction center; it is not making any particular form probable or improbable. It is simply excluding water from the space, thereby altering the effect of the medium; the effect as we observe it, which is a 6000-fold ratio between the first and second ionization constants, is a very large effect and something we may expect to encounter in a number of places in the chemistry of alkyl groups.

Perhaps an extreme case of the space-excluding effect is the situation with the highly hindered phenols, of which tri-*t*-butylphenol is an example. This is a non-acidic compound. In order to make a metallic derivative of this compound it is necessary to dissolve it in ether and treat it with a Grignard reagent or an organo-alkali compound. In no other way can the metallic derivative of it be made, and the metallic derivative is converted by water back into the phenol and the alkali. While the acid strength of this phenol has not been measured, it is certainly powers of ten below that of any ordinary phenol which can be measured in water. The dissociation of an electrolyte into a positive and a negative ion is not a reaction which is subject to steric hindrance. There is nothing about these *t*-butyl groups that is going to prevent the proton from coming off. What then is the nature of the effect of all these methyl groups in depressing the acidity of the tri-*t*-butylphenol? There have been various suggestions, but we can see a certain resemblance between this case and that of tetramethylsuccinic acid. A great deal of space around the negative charge of the anion is occupied by hydrocarbon groups, as shown in Figure 5. We should not expect phenol or anything else to undergo ionization in kerosene as a solvent, and it seems fairly likely that the importance of water as an ionizing solvent consists in access of the water molecules from many directions to the center of the negative charge. If there is only a very limited area in which water molecules can get to that negative charge to solvate it, the tendency which we associate with plain unhindered phenols to ionize is very greatly reduced.

There is one more effect of the methyl groups which

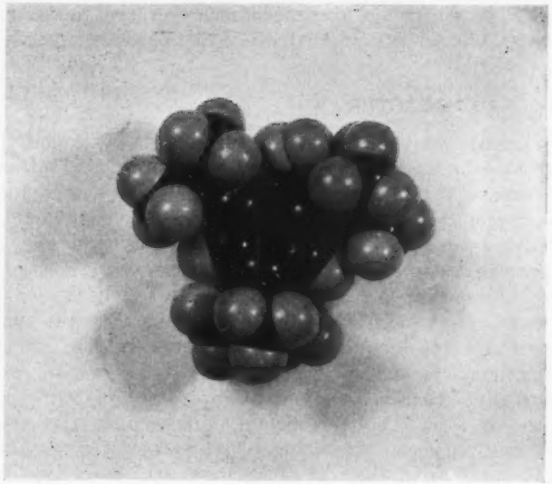
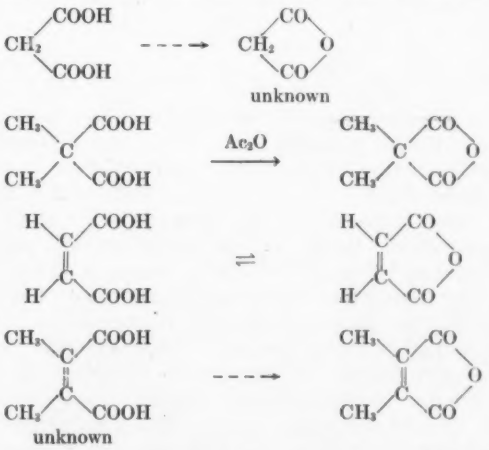


Figure 5

I should like to mention, which is presumably a space effect and which so far as I am concerned is not understood; this is the effect of methyl groups on ring closure, an effect which has been familiar for many years. Malonic acid does not form an anhydride. Dimethylmalonic acid forms a normal anhydride under dehydrating conditions. Another example is given by maleic acid, which changes to maleic anhydride reversibly under dehydrating conditions. We know that dimethylmaleic acid exists in solution because we can neutralize it and make salts of it, but on attempted isolation it forms the anhydride so rapidly that dimethylmaleic acid in the pure state is unknown. We may speculate that perhaps the larger hydrocarbon "cavity" here, in the sense of Kirkwood and Westheimer, makes the dipole-dipole interactions which precede the attack



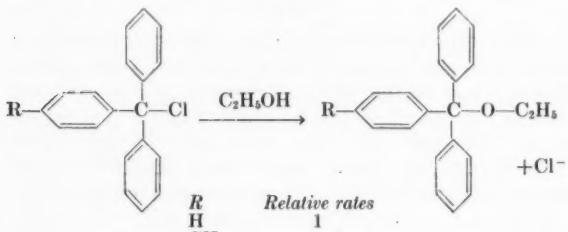

of one group upon the other greater than they otherwise would be, because it excludes a certain amount of water from the neighborhood of the molecule.

The methyl group thus exerts a variety of effects due to its space occupancy. The effects which it can pro-

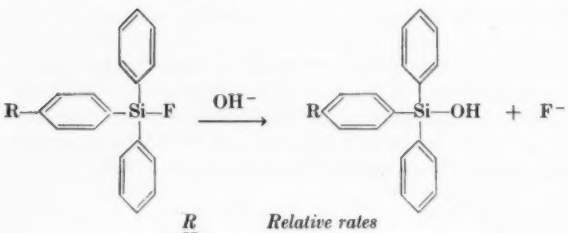
duce depend upon the mechanisms of the reactions which are being examined where the space occupancy is present.

## POLAR CHARACTER

Let us turn now to some of the effects of the methyl group which cannot be explained on the basis of space occupancy. The methyl group, when substituted for hydrogen, sometimes a long way from the seat of the reaction, does influence reaction rates. The standard place to observe an effect like this is the *para* position of the benzene ring. Consider two reactions of compounds that look alike, the ethanolysis of triphenylmethyl chloride and of triphenylsilyl fluoride. Replacement of one of the hydrogen atoms in triphenylmethyl chloride with methyl *increases* the rate of reaction with alcohol fourfold compared to the unsubstituted case. In triphenylsilyl fluoride, the methyl groups *decreases* the rate of reaction with base sixfold.




| *R* | *Relative rates* |
|---|---|
| H | 1 |
| $CH_3$ | 4.1 |

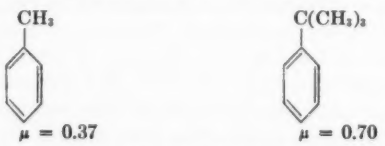



| *R* | *Relative rates* |
|---|---|
| H | 6 |
| $CH_3$ | 1 |

There is one operational difference between these two cases which is readily observed: triphenylmethyl chloride reacts at the same rate whether there is ethoxyl ion there or not. The reaction of triphenylsilyl fluoride proceeds at a rate strictly proportional to the base concentration. Swain (*11*) has accordingly interpreted the opposite effects of the methyl groups in these two cases by saying that the nature of the silicon atom is such that at the transition state in this reaction the hydroxyl group forms most of the bond with the silicon before the fluoride ion breaks off; therefore, in the transition state there is extra negative charge on the molecule and the methyl group has a polar character which is unfavorable to the accumulation of negative charge. With triphenylmethyl chloride, just the reverse is the case. In the transition state the chloride has separated from the carbon to a greater extent than the ethoxyl group has bonded, and this leaves an over-all positive charge on the triphenylmethyl group, to which methyl is favorable. Swain and some of the other current workers in the field of displacement reactions differ in the details of describing the transition state. All would agree that a methyl group in the *para* position is favorable to the appearance of a positive charge and unfavorable to the appearance of a negative charge there.

The same situation is brought out by very simple physical properties of the alkyl benzenes. The dipole moments of toluene and *t*-butylbenzene, for instance, are different by a factor of almost two, *t*-butylbenzene having much the higher dipole moment. It has been shown by pitting one group against another in the *para* positions of the benzene ring that the dipole of an alkyl-substituted benzene has its negative end in the ring and the positive end outside the ring, meaning that all alkyl groups have an electron-releasing effect toward the benzene ring. Therefore this is bound to be favorable toward reactions in which a positive charge is to be accommodated in a side chain on the opposite side of the benzene ring. The release of electrons toward the ring will mean that a positive charge can be effectively distributed over a greater space than without the alkyl group. This is something common to both the methyl and *t*-butyl groups. The fact is familiar but the explanation is not obvious. An alkyl group, when bonded to another alkyl group, obviously balances and shows no particular tendency to attract or release electrons. Why then should it develop this polarity when bonded to an unsaturated group or to a phenyl group?

Another problem, beside the general one of the nature of this electron-releasing effect, concerns the difference between toluene and *t*-butylbenzene. There have been many experiments performed in which the methyl group and the *t*-butyl group have been compared in their effects at the *para* position of the benzene ring, and it is found very often that in certain reactions the *t*-butyl group, which produces the higher dipole moment, produces the smaller effect upon the reaction rate. The bromination of the alkylbenzenes in the *para* position, worked on extensively by Berliner (*12*), is a case in point. Both toluene and *t*-butylbenzene brominate in the *para* position a great deal faster than benzene brominates in any single position; if this is to be associated with the election-releasing properties of the groups, as indeed it must be, one would think that the group which, judged by dipole moments, is the most effective electron-releasing group, and would most greatly enhance the rate; but that is not the case. The methyl group gives a 5.6-fold faster bromination in the para position than does the *t*-butyl so that we are




Relative rates of bromination in para position:

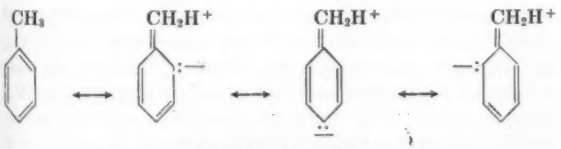
| | |
|---|---|
| 5.6 | 1.0 |

confronted, as far as the polar character of the methyl group is concerned, with explaining two things: Why is there any polar effect at all, why is there any electron-releasing effect; and second, why is the electron-releasing effect as observed in reaction rates and other means not thoroughly consistent with the electron-releasing effect as determined by static methods such as the dipole moment? This is something with which anyone who works with homologous series sooner or later becomes concerned.

## THEORIES

Two chief explanations have been offered for the electron-releasing effect of alkyl groups; the first is the simple inductive effect, and this is more a name than an explanation. It has been considered since the earliest days of the electronic theory of organic reactions, and it is one of the axioms of Robinson and Ingold in their orderly discussion of the phenomena of substitution in the benzene ring, that the methyl group is inherently electropositive relative to the benzene ring, just as chlorine is electronegative relative to carbon. It is a further postulate of the theories of Robinson and of Ingold that when this electron release by methyl takes place in the number 1 position of the benzene ring, the effect is relayed around the ring to the 2- and 4-positions by what then resembles a resonance effect. This effect of alternating electron densities is a very common accompaniment of any resonance effect, but it was an important part of the Robinson and Ingold theory that the effect might be started out inductively and relayed by a resonance mechanism around the ring, so that the effect of the methyl group or some other group would appear in an alternating manner and the pattern of the charge distribution would not reveal whether it arose from a resonance effect or from an inductive process.

Inductive effect (Robinson, Ingold)

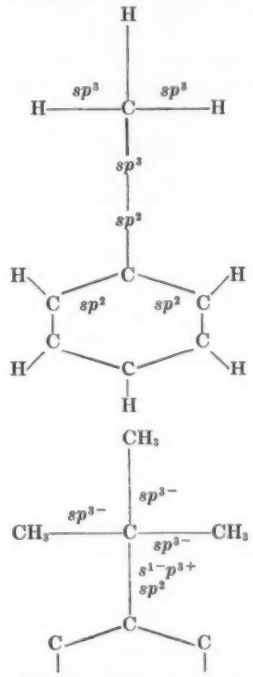



Baker-Nathan effect

The other explanation that has been advanced for the effect of alkyl groups, and particularly of methyl groups, is the one proposed by Baker and Nathan, involving what has sometimes been called "no-bond resonance" and now more generally included under the heading of "hyperconjugation" (*13*). This takes advantage of the potential polar character of the carbon-hydrogen bond to represent structures in which the electron pair which bonds hydrogen to carbon has been reallocated in much the same manner as the electron pair on the amino group in aniline. Being originally a resonance effect, that would definitely result in alternating electron densities around the ring.

## DISCUSSION

The question may well be asked: "How can there be an inherent inductive effect in the methyl group?" The only answer that seems to me at all satisfactory is the one advanced by A. D. Walsh (*14*) based on continuous rehybridization of bond orbitals. The *s*-orbital and *p*-orbital are concepts which come from the wave mechanics of the hydrogen atom; it is assumed that all of the atoms with which we deal in organic chemistry have *s*-orbitals and *p*-orbitals, and that when carbon is saturated, each orbital is a hybrid made up of one part *s* and three parts *p*, these hybrid orbitals having a tetrahedral distribution in space. A model structure for toluene is shown below.




As far as the methyl carbon is concerned, the orbital which bonds this carbon to the ring is a strictly $sp^3$ orbital. However, as far as the benzene ring is concerned, each fixed bond between the carbons and each bond joining the carbon to a hydrogen or a side chain is only $sp^2$ hybridized, coplanar with angles of 120°. There is left over a *p*-orbital—one for each carbon atom here—which unite to give the much-discussed $\pi$-orbital system of benzene. The *s*-orbital is spherically symmetrical so that the center of distribution of the electrons is closer to the nucleus than that of the *p*-orbital; this should mean that when the *s*- and *p*-orbitals are hybridized, the greater the proportion

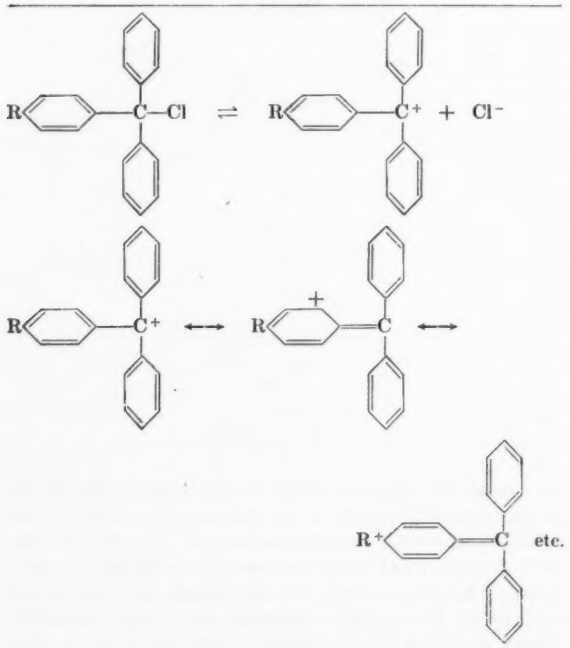
**TABLE 3**
**Ionization Exponents of Acids with *m*- and *p*- —$N(CH_3)_3^+$ Groups (Roberts)**

| *Acid* | *No substituent* | *m*-$N(CH_3)_3^+$ | *p*-$N(CH_3)_3^+$ |
|---|---|---|---|
| $RC_6H_4COOH$ | 5.71 | 4.22 | 4.42 |
| $RC_6H_4NH_3^+$ | 4.57 | 2.26 | 2.51 |

of *s*-character in the resulting orbital, the more electronegative the atom which has that orbital is going to be in its bonds, so that an $sp^2$ orbital in a ring carbon atom should pull the electrons toward it more than an $sp^3$ orbital in the carbon of the methyl group. That is a sufficient basis for the polar character of the methyl group, not only when it is bonded to benzene, but in any case in which it is bonded to a carbon with $sp^2$ hybridization. It works out consistently. Substitution of a phenyl group into a saturated compound in place of a methyl group or in place of a hydrogen appears to exhibit an electron-attracting effect, which is due to exactly the same cause.

Now we can compare the methyl group and the *t*-butyl group and see a tendency that might account for the greater inductive effect of the *t*-butyl group. The *t*-butyl group is that group which, compared to methyl, forms a coplanar carbonium ion well and assumes a positive charge on the central carbon. This means that these three methyls of the *t*-butyl tend to spread out toward the 120° bond angle. They cannot do so as long as the central carbon atom has $sp^3$ (tetrahedral) orbitals, but the tendency would always be toward a little less *p*-character in each of these three bonds, tending to flatten and go to the ideal of $sp^2$. The bond to the benzene ring will not be perfectly $sp^2$ either, and will have a little more *p*-character even than the bond which comes from the methyl group. Hence the higher dipole moment inherent in this structure.

**TABLE 4**
**Ionization Constants in Liquid Sulfur Dioxide (N. N. Lichtin)**




| *R* | $10^5K^{0°}$ | $\Delta F^{0°}$ | $\Delta\Delta F^{0°}$ | *Estimated effect* *Inductive* | *Resonance* |
|---|---|---|---|---|---|
| H | 4.03 | +5.49 | | | |
| *m*-$CH_3$ | 9.2 | 5.04 | −0.45 | −0.45 | 0 |
| *p*-$CH_3$ | 71.0 | 3.93 | −1.56 | −1.54 | −1.02 |
| *m*-$(CH_3)_3C$ | 16.0 | 4.74 | −0.75 | −0.75 | 0 |
| *p*-$(CH_3)_3C$ | 76.0 | 3.90 | −1.59 | −0.90 | −0.96 |

Another question is: "What is the basis for the postulate that the inductive effect produces alternating electron densities around the ring?" This has recently been attacked by J. D. Roberts (*15*) in a comprehensive fashion. Roberts has examined a type of compound—a series of benzene derivatives with trimethylammonium groups—which has a powerful electrostatic pull of electrons from the ring to the charged group, but no classical resonance mechanism of electron displacement. This group is placed in the *meta* and *para* position to a carboxyl group or to an amino group and its effect on the ionization constants of these compounds is observed. If the electron deficiency which is produced by the pulling effect of the trimethylammonium group on the ring is relayed preferentially to the *ortho* and *para* positions, this group should be more powerful in the *para* position than in the *meta* position. On the other hand, if the inductive effect simply falls off around the ring, it should be more effective in the *meta* position than it is in the *para* position. Table 3 shows the ionization exponent for benzoic acid without a substituent, with a *m*-trimethylammonium group and with a *p*-trimethylammonium group. We see that less change has been made by putting the group in the *para* position than by putting it in the *meta* position. The same is true if we compare the ionization constants of the corresponding anilines; they decrease more for substitution in the *meta* position than in the *para* position. These results show that it is not true that alternating electron densities are produced by an inductive effect in the benzene ring.

We have tried to take advantage of this in the material shown in Table 4 in accounting for the effects of methyl and *t*-butyl groups on an equilibrium involving an organic cation, the well-known reaction of the ionization of triphenylmethyl chloride in liquid sulfur dioxide (*16*). The ionization constant of triphenylmethyl chloride in liquid sulfur dioxide can be measured quite accurately; we have done this for a number of compounds, including plain triphenylmethyl chloride, *m*-methyl, *p*-methyl, *m*-*t*-butyl, and *p*-*t*-butyl, and the results are quite clear with respect to the relative characters of these two groups. Incidentally, the assigning of an ionization constant is an interesting process because the dielectric constant is so low that one has to make corrections for activity coefficients and use a more elaborate treatment of the data than one

would use in water. We translate these ionization constants into free energy changes for ionization and then we take the effect of substitution on the free energy change; this increment is represented by $\Delta\Delta F°$ at 0°. This is the amount by which the free energy of ionization is rendered less positive by the introduction of these various groups. When we compare the methyl group and the *t*-butyl group in the *meta*-position, we find that both of them enhance the ionization of triphenylmethyl chloride, but the *t*-butyl group produces substantially more effect in terms of free energy change than the methyl group in the *meta*-position. We might conclude that, as a *meta* substituent, the *t*-butyl group is a far more powerful polar group than the methyl. What kind of electronic influence can be exerted upon the seat of reaction from the *meta* position? We have seen that no resonance effect can be. The *meta* positions on the benzene ring are an effective filter for removing resonance effects. Since it has been shown that the inductive effect falls off in an orderly way, the inductive effect might be expected to be rather stronger in the *meta* position than in the *para*. We conclude, as we already know from dipole measurements, that the *inductive* effect of the *t*-butyl group is considerably greater than that of the methyl group. Now, in the *para* position the methyl group produces a difference of 1.56 kg.-cal. and the *t*-butyl group of 1.59 kg.-cal.—very close to one another—in fact, probably within the experimental error of the determination. This means that when we move them around to the *para* position, the methyl group has overtaken the *t*-butyl and whatever effect it is that can exist in the *para* position and not in the *meta* position is one in which the methyl group excels the *t*-butyl.

If we adopt the view of Roberts that the inductive effect falls off steadily around the ring, while the resonance effect is relayed preferentially to the *ortho* and *para* positions, we can try to resolve the effect of these groups, and if we estimate the inductive effect of the methyl group by taking it to be that at the *meta* position, we get 0.45 for an inductive effect there and 0.75 for an inductive effect of the *m*-*t*-butyl group. The resonance effect or the Baker-Nathan effect is then the difference between these inductive corrections and what is observed in the *para* position. We should make a small correction for the falling off between the *meta* and *para* positions, but it is almost negligible. If we now take the difference between what is observed for the *p*-methyl compound and what we estimate to be the inductive effect, we get 1.02, and if we do the same for the *t*-butyl, we get 0.69. This means that the Baker-Nathan effect is present in both the methyl and the *t*-butyl. We do have hyperconjugation of the methyls in the *t*-butyl group, but it is not quite as effective as hyperconjugation of the hydrogen atom, and so the confusing results, which are observed in a great many reactions where the methyl and the *t*-butyl are compared, are easily understood. The methyl has a weaker inductive effect and a more powerful hyperconjugative effect than the *t*-butyl, and every new reaction that one examines will be susceptible in different degrees to these two effects.

As with many other simple problems, the chemical properties of the methyl group have led into varying aspects of stereochemistry, reaction mechanisms, and the nature of the chemical bond. In turn, the fundamental principles established in the pursuit of this problem are of use in the approach to other questions of a more complicated nature.

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## MIDWINTER MEETING OF NJSTA

The midwinter conference of the New Jersey Science Teachers' Association will be held at State Teachers' College, Jersey City, on Saturday, February 7, at 9:00 A.M. The program will be Visualizing the Visible (materials for visual aids). Dr. Catherine Bergen of the college staff will direct the meeting.

# GLASS: HISTORICAL NOTES, 1900 TO 1950[1]

**ALEXANDER SILVERMAN**
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THE first half of the twentieth century has experienced such extraordinary development in the manufacture and use of glass that it might appropriately be referred to as the "Glass Age." Scientific research has played an important part; chemists, physicists, and engineers deserve special commendation.

*Window Glass.* While Theophilus, an Anglo-Saxon monk of the twelfth century, is said to have blown, cracked, and flattened the first hand-blown cylinders, and while Lubbers had mechanized the process during the latter part of the nineteenth century for the blowing and drawing of cylinders 30 inches in diameter and 30 feet long, the production of continuously drawn sheet-glass awaited the coming of the twentieth century.

In 1902 Emile Fourcault of Belgium invented a process for drawing glass vertically from a tank through a *debiteuse*, or slotted refractory block which floated on the molten glass surface, and through its own weight forced glass through the long narrow opening. The sheet was then raised vertically between rolls, and was annealed by the convection currents created by its own cooling. The glass was cut into suitable lengths at an upper level.

In 1903 Irving W. Colburn, an American, independently invented a sheet-drawing machine. An iron bar started a sheet on lowering it horizontally into a tank of glass and then raising the bar. The vertically rising sheet was heated and allowed to travel horizontally over rolls into annealing ovens. The Colburn process had the advantage of handling the glass at the ground level, while the Fourcault process did not require annealing fuel. There have been numerous modifications and improvements of the original inventions, such as the submerged *debiteuse*, cooling control of the sheet, greater homogeneity during melting, etc., etc.

The old hand-blown glass distorted the images of objects viewed through it. Machine-made cylinder glass still distorted them, but less. Quality improved with the advent and development of sheet machines and their control, and some of these now produce window glass almost as perfect as ground and polished plate glass.

According to information graciously furnished by Arthur W. Kimes, Editor of the *National Glass Budget*, there were 107 individual factories in the United States in 1900 for making hand-blown window glass. In 1950 very few remained—only an occasional plant to satisfy a special demand. In 1949 America had only 15 sheet glass plants because manufacture had been mechanized.

[1] Presented at the 122nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1952.

It must not be assumed that the engineer alone was responsible for the evolution and improvement of window glass. With gas firing and the more recent electric melting, the chemist's improved composition and the physicist's controls, and with better furnace materials, the product competes favorably with plate glass.

*Plate Glass—Hollow Tile.* The pouring of a pot of glass onto a casting table and passing a roller over the glass started at Saint Gobain in France in 1688, the invention of Lucas de Nehou. Early American practice was similar. There was, however, one difference. In France members of the nobility could work in glass plants without losing caste; glass workers could intermarry with the nobility; glass workers were exempt from taxation. While we are no longer interested in the caste system and may not wish to intermarry with the nobility, we should all appreciate tax exemption.

During the first half of the twentieth century the casting of plate glass from pots continued, but later gave way in part to the Bicheroux Process, in which glass is poured from larger pots of eliptical cross-section between rolls, letting the plate descend onto an inclined polished steel table and then travel horizontally in the usual manner through annealing ovens to the grinding and polishing tables.

While the Nehou and Bicheroux processes are still in use, plate glass is made continuously by running glass through rolls from a tank furnace, then annealing, grinding, and polishing.

From the older cast glass, plates were transferred to grinding and polishing tables. In the continuous-sheet process they traveled directly onto grinding and polishing tables, being cut into suitable lengths during their journey and later turned over for grinding and polishing on the reverse side. Now a method has been invented for grinding and polishing simultaneously on both sides.

Gas firing and annealing have been replaced wholly or in part by electrical operations which afford better control, especially localized control.

Precision grinding and polishing have brought almost unbelievable uniformity of surface level. A study of polishing materials has established the significance of crystal form. Plate glass has been tempered by suitable heating and chilling. The early-century wired glass has in turn given way to plastic lamination and to laminated tempered plate. Glass of all thicknesses and of incredible mechanical strength—for example for use in aviation—has resulted.

Ordinary wet-silvered mirrors, now made practically free from pinholes in some factories, have given way in

part to metallized surfaces of aluminum, chromium, etc., condensed on the cold glass in vacuum compartments. These near-side mirrors, especially of aluminum, reproduce images in more nearly perfect colors than the old far-side silver mirror. Both silver and chromium mirrors may be applied so thin as to possess various degrees of transparency, obscuring the viewer on the dark side of the mirror, yet permitting him to see through to the light side.

Although plate glass in black, white, and other colors was produced in limited quantity before 1900, it is now a regular part of structural glass supply.

Hollow tile is foreign, in manufacturing principle, to plate glass, but, like clear and colored plate and glass tile, is used extensively in building. In most factories the halves of the hollow tile are pressed separately and then stuck or welded together. The surfaces may be clear, prismatic, or irregular. Diffusing materials may be placed between the halves. The contained air is a good insulator. Like plate and window glass the product may be colored green by ferrous iron, further to absorb heat.

In 1900 there were nine polished plate glass factories in the United States and eleven that manufactured Cathedral rough plate and tile glass. In 1950 there were only eight polished-plate factories but their production was much greater, as some of these rolled continuously direct from tanks; also, there were eleven factories that made rolled, wired, figured, and colored sheet glass.

*Bottles, Jars, Containers.* Prior to 1900 bottles were generally blown by hand, or at least gathered by hand and then blown in molds. The necks were usually shaped separately. In 1882 Arbogast formed a complete bottle in a mold by pressing. In 1903 Michael Owens invented the bottle machine which now produces all sizes and shapes. Some modern machines (Owens and later inventions) have 24 arms. The glass is either sucked into the molds or dropped in the form of gobs One factory produces over a million beer bottles each day. The bottles travel continuously to the lehrs on belt conveyors, and some of the lehrs are so well insulated that bottles are annealed by their own heat. In addition to the standard colorless, amber, and green bottles there are a number of colors; also there are many fancy containers for perfumes, lotions, etc.

At the turn of the century we had 156 bottle factories in the United States. The number has dropped to 97 but mechanization has increased production enormously. Besides, the one-way bottle has arrived, a thinner-walled container which may not be returned for re-use. This will further increase production.

*Electric Lamp Bulbs and Tubes—Illumination.* Originally blown by hand and later in molds, the bulb followed the trail of the bottle, and the Westlake bulb machine became about as famous as the Owens bottle machine. In 1927 a new machine formed a ribbon which had lenslike elevations from which blow-heads formed the bulbs. The glass for lamp bulbs has been perfected to a degree where it is practically flawless, and almost-mechanical methods have been developed for etching and otherwise roughing their interiors to insure good diffusion and transmission of light without producing harmful glare. In addition to ordinary bulbs there are flashlight bulbs, the blue (daylight) bulbs, yellow (insect-repelling) lamps, sun lamps, infrared lamps, X-ray bulbs; radio, television, and radar bulbs. Nor dare we overlook the mercury-arc tube lamps. One, the size of a cigarette, is a 1000-watt lamp. The intensities can be vastly greater. The heat generated demands water cooling. Also we have the two-billion candle power beam, and the neon-filled and special-atmosphere lamps for airplane beacons and landing fields.

Sodium-vapor lamps, sterilamps, both bulb and tube, and the many fluorescent coated tubes, all of which contain mercury vapor, must be included and while neither bulb nor tube, we cannot overlook the fluorescent laminated sheet glass which is the latest member of the electric lighting family, and which will furnish subdued illumination from ceiling and walls.

As the writer has often said, "We may have anything from sunrise to moonlight, any color of the rainbow, any special therapeutic rays in our homes, that we wish and that we can afford. We can cater to our whims and moods; we can benefit from health-giving radiations."

The half-century has enabled us to record radiations from the highest to the lowest frequencies though our unaided eyes can detect only a small fraction of these.

As bulb and tubing plants are not listed separately for 1900 and 1950 but are in a miscellaneous group which includes lighting and tableware, building block and other blown and pressed ware, statistical comparison is not feasible.

*Table Ware and Art Glass.* Table ware has evolved from the handmade, paste-mold, iron-mold, and simpler pressed articles to the mass-produced, machine-made articles now available even in the so-called "5 and 10 cent stores." Early in the Christian Era "only the King and nobility drank from glass." Today everyone does. The cool touch of glass to the lips has some competition from the warmer insipid feel of plastics. For the writer the latter can never replace glass.

Borosilicate glass of the laboratory is used as ovenware and doors, and in top-of-stove ware because of its low coefficient of expansion and its high thermal and mechanical shock resistance. Glass has been made in more than 50,000 color tones. Our crystal is colorless.

Etched, incrusted, enameled, and iridescent glasses are so common as almost to escape notice. Yet they are in many instances more attractive than in the days when few could afford them.

In addition to the inspiring stained-glass windows of the modern churches, we have superb sculptures in public structures. Mosaics, once the exclusive possession of the house of worship, adorn the walls of railroad station and office building. The creations of artist and artisan are not restricted to the wealthy; industrial art, produced in quantity, is available for every man.

Outstanding among the art glass creations of this period is the so-called "photosensitive glass," which contains gold, silver, and other substances in solution. On exposure to arc-light through a negative or mask, and subsequent heating near the softening-point of the glass, the print develops in the interior of the glass and is permanently recorded in colloidal form and various colors depending on particle sizes.

*Optical Glass.* In this division progress has been very marked. Although very few elements and their compounds were in use prior to 1880, and although Ernst Abbé and Otto Schott increased the number of elements beyond 25, the last 50 years have brought us glasses which contain practically all of the chemical elements except the harmfully radioactive ones. The index of refraction has approached 2.0 and the dispersion has been lowered greatly. In the dark-glass field for spectacles we have evolved from the old smoked, amber, and Crookes' glass (1905) to a variety of colors that not only protect the eyes but in special instances match milady's gowns. Recently, glasses have been developed which absorb harmful high-energy X- and gamma-rays and slow neutrons. These should be useful for protecting workers in atomic energy plants, and the public generally in case of atom-bomb attacks.

Optical glass must be considered from the aspect of size as well as composition. In this respect we consider the 200-inch reflector on Mount Palomar in California, which has enabled astronomers to study in the universe many galaxies beyond the limits of earlier astronomical possibility.

Under optical glass we should also include compositions which permit the absorption or transmission of radiations of special wave lengths. Glasses are available which render this service for waves from the shortest to the longest. During World War II glasses were produced whose transmitted flood light camouflaged war craft by day as well as by night. It was during the period 1900–50 that the United States acquired both independence and supremacy in the manufacture of optical glass.

*Laboratory Ware.* Before World War I it was common practice to import laboratory ware from Europe. Then the embargo on exports to America made us resourceful. Not only had we produced alkali-resistant glass at the beginning of the century, but later researches brought high borosilicate glasses which surpassed the famous ware that had previously been imported. Transparent fused quartz had been melted in pressure-vacuum electric furnaces. Then high borosilicate glasses were leached chemically and the extracted masses reheated to yield high-silica ware, 95 per cent or higher in $SiO_2$, which has not only replaced quartz in part but opened new avenues in science and industry. Among the phosphate glasses of the half-century is one which resists the action of hydrofluoric acid and another that is a colorless ferrous-iron heat absorber.

*Fiber Glass and Foam Glass.* Perhaps the most phenomenal growth in the glass industry has been in the fiber-glass field. So many new factories have been built recently that one may expect a new announcement almost any day on the financial pages of our daily papers. A variety of types of fiber glass is now available from the ordinary lime glass beginnings to almost pure silica threads. The uses range from thermal and electrical insulation through plastics-reinforcement, textile manufacture, and even surgical applications. The micron and submicron have entered the field of filament diameters.

Foam glass is an important insulator and structural material. Both foam glass and fiber glass are rodent and vermin proof.

*Miscellaneous.* Feldspar has been replaced, wholly or in part, by nepheline syenite, aplite, kyanite, lepidolite, and other silicate minerals in glass batches. Alumina has been substituted for silica. The silicones have been applied as bonding agents and for surface treatment.

Solarization has been prevented through use of decolorizers like cerium and neodymium compounds and omission of arsenic compounds.

Sheet and fiber glass have been used as molten lubricants in the drawing of steel to prevent mold erosion.

Studies have been made on variations in transmission and absorption with changes of temperature.

Considerable knowledge has been added concerning diffusion of metals and gases through various glasses.

Glass has been formed from vapors, and various vapors have been applied to glass to impart special properties, such as surface conduction, etc.

Tubing has been made up to 4-inch diameter and perhaps larger. It has been welded and coupled, and many miles have been used in beverage plants and in modern construction.

Phase-equilibrium studies have been conducted on two-, three-, and four-component systems of glass-forming substances.

Coefficients of thermal expansion, density, and refraction data have been corrected through experiment and through the application of theoretical data.

Considerable light has been thrown on the nature and causes of glass fractures.

Synthetic rubies and sapphires and special glasses for jewel-bearings have been made in America.

Durability of glass has been improved.

Studies have been made of the effects of temperature, atmosphere, and composition on the production and striking of opal glasses.

Studies and researches have accounted for color in and absorption by iron, selenium, and other glasses.

Beads are manufactured by blowing glass fragments through hot atmospheres that melt and round them.

Last and perhaps most important, the structure of an increasing number of glasses has been determined. With knowledge concerning glass formers, glass modifiers, ionic and atomic radii, bond strengths, etc., glass properties can be estimated in advance and the nature of the resulting glasses can be predicted with almost unbelievable accuracy.

# FRAGMENTS OF CHEMISTRY

**CHARLES A. KRAUS**
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## 9. EQUILIBRIA BETWEEN METALS AND SALTS[1]

Some 20 years ago E. Rink[2] investigated the equilibria of sodium and potassium in the presence of $OH^-$, $F^-$, $Cl^-$, $Br^-$, and $I^-$ ions. He also investigated the equilibria of sodium and calcium in the presence of chloride ion.

When sodium is added to fused potassium chloride, sodium and potassium appear in both the metal and the salt phases. The metal phase is the richer in potassium the smaller the proportion of sodium added. On reacting one atom of sodium per mol of potassium chloride at 900° C., the metal phase contains 25.5 atom per cent K; on adding 0.5 atom Na, the metal phase contains 83.1 per cent K.

The distribution of Na and K between the metal and salt phases depends on the nature of the negative ion. With a Na/K ratio of 1, the metal phase, with fluoride ion, contains 65 atom per cent K, with chloride ion, 25 per cent, with bromide ion, 15 per cent, and with iodide ion, 12 per cent. Using salts in the fused state, the distribution of the metals is little affected by temperature.

(1) *The Na–K–S System.* Reaction between metal and salt takes place quite as readily with crystalline as with fused salts, perhaps even more readily. Reaction occurs at temperatures as low as 450° C. The potassium and sodium halides form mixed crystals. Accordingly, the composition of the salt phase varies as the ratio Na/K is varied. Sodium and potassium sulfides do not form mixed crystals and it follows that the composition of all phases is fixed if the temperature is fixed.

The reaction between sodium and crystalline potassium sulfide takes place in two stages. For the ratio $Na/K < 0.5$, we have the reaction:

$$K_2S + Na \rightarrow NaSK + K \qquad (1)$$

For $Na/K > 0.5$, we have

$$NaSK + Na \rightarrow Na_2S + K \qquad (2)$$

Here we have three components and four phases and, therefore, at constant temperature, the composition of all phases is fixed.

Before detailing the two equilibria above, a few words might be said about potassium sulfide. This compound may be prepared in the pure state by reacting the metal with sulfur in liquid ammonia. The sulfide is obtained as a fine, white powder. This powder ignites in air and is thereby heated to incandescence. It is interesting to note that here we have a case of flameless combustion. It is not known what the products of combustion may be. Potassium sulfide may be produced by reduction of potassium sulfate with carbon at 1000° or by illuminating gas in the presence of carbon at 850°. However, the conversion to $K_2S$ is not complete. On treating the product with sodium, not all the potassium is recovered as metal unless a large excess of sodium is used.

With the pure molten salt, using two atoms of sodium per mol of $K_2S$ at 900° C., the metal phase contains 62 atom per cent K. With two atoms of sodium per mol of $K_2S$, solid, at 600°, the alloy contains 83 atom per cent K. For the production of potassium-rich alloys, the equilibrium with solid phases is much more favorable than is that with the liquid phases.

For a ratio $Na/K < 0.5$, at 600°, the alloy contains 96 atom per cent K. The phases are $K_2S$, NaSK, liquid, and vapor. For a ratio $Na/K > 0.5$, the metal phase contains approximately 70 atom per cent K and the phases are NaSK, $Na_2S$, liquid, and vapor. If the metal is distilled using one atom of Na per atom of K, the alloy will have the mean composition of 83 per cent K, since the composition of the metal phase of reaction (2) is 70 per cent K. There is evidence that the compound NaSK is formed when $K_2S$ is treated with less than one atom of Na per mol of $K_2S$ in liquid ammonia.

With decreasing temperature the alloy phase becomes richer in K. Thus, on adding 0.75 atom of sodium per equivalent of $K_2S$, the alloy phase has the composition as indicated below at different temperatures. The temperatures are those of the furnace and are approximately 50° higher than the temperature of the reactants. The melting point of $K_2S$ is approximately 850°.

| $t$°C., furnace | 500 | 550 | 600 | 700 | 750 | 800 |
|---|---|---|---|---|---|---|
| at. % K in alloy | 95.5 | 93.9 | 89.5 | 83.3 | 79.3 | 73.2 |

Since the alloy of equilibrium (1) already contains 96 per cent K at 600°, the enrichment of the alloy at lower temperatures must be due to a pronounced shift of equilibrium (2) toward richer alloy.

What the factors are that govern the composition of the salt and metal phases under different conditions of temperature we do not know. In view of our lack

[1] During the period 1940–42 various equilibria between metals and salts were investigated in the Brown Laboratories for the Naval Research Laboratory. The results of these investigations have not been published heretofore. They are briefly summarized here.

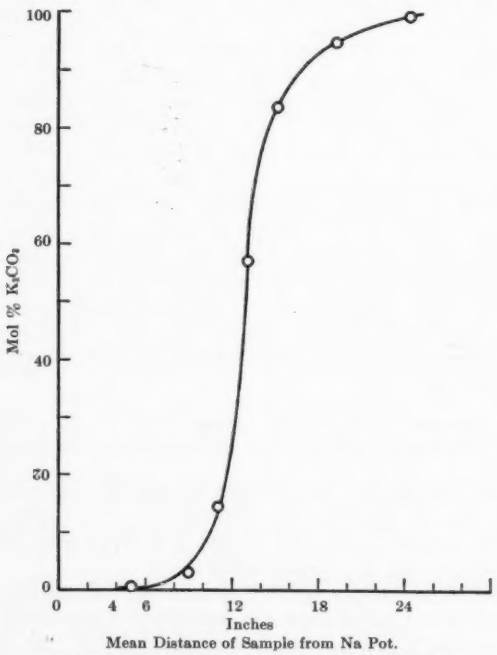
[2] *Ann. chim.*, **18**, 395 (1932).

of knowledge in this field it is idle to speculate. It may be pointed out, however, that we are here dealing with certain fundamental aspects of both salts and metals. It would be of interest to know something of similar equilibria involving rubidium and cesium. It would also be of interest to know something of equilibria involving selenium or tellurium in place of sulfur. Other systems in which the sodium and potassium salts did not form mixed crystals would also be of interest.

(2) *The System K–$CO_3$–Na.* The carbonates of potassium and sodium form a complete series of mixed crystals having a minimum melting point of 704°C. at 45 mol per cent $K_2CO_3$. It follows that the metal phase in equilibrium with the solid phases will have a varying composition depending on the Na/K ratio. The carbonate ion is stable with respect to sodium and potassium in the solid state. Its stability in the liquid state has not been investigated.

With a Na/K ratio of 1.0, the alloy at 600° contains 67.7 atom per cent K. For the ratio Na/K = 0.5, the alloy at the same temperature contains 90.8 atom per cent K. With decreasing Na/K ratio, the percentage of potassium in the alloy in the presence of carbonate ion increases more than it does in the presence of the fluoride ion. For a Na/K ratio of 1.0 the alloy in the case of fluoride ion contains 77.8 atom per cent K, as against 67.7 per cent for carbonate. However, for a Na/K ratio of 0.5, the alloy contains 86.2 per cent K for fluoride and 90.8 per cent carbonate.

As in the case of the sulfide, the potassium content of the alloy in the carbonate equilibrium increases with decreasing temperature. Thus, for a Na/K ratio of 0.75, the alloy contains 69.7 per cent K at 650° and 92.5 per cent K at 550°. For a Na/K ratio of 0.5, the alloy contains 79.5 per cent K at 650° and 94.0 per cent K at 550°. It should be noted that these are furnace temperatures and that the temperature of the reactants is approximately 50° lower. For a Na/K ratio of 0.8, the alloy contains only 71.9 per cent K at 500° (furnace), and 94 per cent K at 550°. This low content of K at 500° may be accounted for in that, at 490°C., the mixed crystals begin to separate into two phases, the composition of which diverges rapidly with decreasing temperature.




**Distribution of $K_2CO_3$ in Column at End of Reaction**

Values given for the composition of the metal phase are for reactions where the metal is well distributed throughout the mass of carbonate (in the form of pellets or small lumps). If the metal (Na) is placed underneath the carbonate so that its vapor passes through the mass of crystalline material above, an enrichment process occurs and the metal as collected is much richer in K than it otherwise would be. For example, with KF and a Na/K ratio of 1.0 at 600°, the alloy as collected contained 77.8 atom per cent K when the Na was placed on top of the salt; when the metal was vaporized from a cup underneath the salt, the alloy contained 87.7 per cent K.

The reaction between the liquid metal phase and the solid salt phase is a rapid one. If metal vapors are passed over the salt at a temperature higher than that of the vapors, only appreciable enrichment occurs. When, however, the salt is at a lower temperature than the vapor so that condensation occurs, great enrichment takes place. For example, on passing an alloy containing 85 atom per cent K through a column of $K_2CO_3$ at the rate of 15.9 g./min. with the boiler at 550° and the column at 625°, the alloy as collected contained 88 per cent K. In another experiment, passing vapor at the rate of 21 g./min., with the boiler and column temperature at 550°, the alloy as collected contained 98 per cent K.

Sodium and potassium, as well as their alloys, wet solid salts. If the temperature of the salt is below that of the vapor, the latter condenses on the solid and interacts with it. The enriched metal (in K) vaporizes to condense again on other salt particles, and the enrichment process continues until the metal phase consists of practically pure potassium. The heat of formation of $K_2CO_3$ is somewhat less than that of $Na_2CO_3$ so that the conversion from the potassium to sodium salt tends to absorb heat.

A column was packed with 25 inches of $K_2CO_3$ in granular form. One equivalent of sodium per mol of $K_2CO_3$ was put in a boiler underneath the column and the vapor was passed over the salt in the column. When all the sodium had been volatilized and the reaction products collected, the salt in the column was removed in sections and analyzed for its $K_2CO_3$ content. The results follow and are shown in the graph.

Temp. of column, 550°. At. % K in product, 99.4.

| Distance of salt from boiler, in. | 5 | 9 | 11 | 13 | 15 | 19 | 24 |
|---|---|---|---|---|---|---|---|
| Mol % $K_2CO_3$ in salt | 0.5 | 3.0 | 14.4 | 57.0 | 85.5 | 94.6 | 99.1 |

As may be seen from the table and more readily from the figure, the solid salt acted as a very efficient fractionating column. The lower half of the column retained only 7 mol per cent of potassium and the upper half correspondingly contained 7 per cent of sodium. The last section contained 99.1 mol per cent $K_2CO_3$ and the metal collected contained 99.4 atom per cent K.

In studying the enrichment process, the potassium carbonate was employed in the form of granules or lumps from $^1/_6$ to $^1/_2$ in. diameter and varied in bulk density, as packed, from 0.41 to 0.75. These factors were found to have little effect on the potassium content of the alloy produced.

(3) *Some Other Reactions for Producing Potassium.* Potassium is produced by the reaction of various metals with potassium sulfide. These require a temperature of 1000° or more. With iron and aluminum, yields obtained are at best 50 per cent of theoretical. With magnesium, higher yields are obtained but the volatility of magnesium is disadvantageous, particularly if reaction is carried out under vacuum conditions.

Calcium carbide and calcium silicide react with $K_2S$ and KF to yield potassium. Potassium is produced when $K_2S$ is reacted with $CaC_2$ or $CaSi_2$ at 1000° *in vacuo*. The yield is not above 50 per cent.

With KF, calcium carbide and calcium silicide react readily above the melting point of KF. Under suitable conditions, the yields are quantitative. Nitrogen tends to react with the carbide or silicide at 1000°. With calcium carbide there is appreciable dusting of carbon; with calcium silicide the condensed metal has a clean surface. The reaction of $CaSi_2$ with an alkali metal fluoride might prove useful in preparing cesium and rubidium.

Indications are that $K_2C_2$ and $K_2Si_2$ are formed as primary products in the reaction of KF with the corresponding calcium compounds. When KF is reacted with $CaC_2$ at 825°, 70° above the boiling point of potassium, no potassium comes over until the pressure is reduced to about 15 cm. Similar observations have been made in the case of silicon. Further study of these dissociation phenomena would be of interest. The state of the silicon resulting from the reaction of $CaSi_2$ with KF is not known.

## TEACHING SCIENCE IN AFGHANISTAN

THE following extracts from a letter by Clifford S. Benton were sent to us from Dr. N. D. Cheronis, who received it. Our readers will be interested.

Kabul, Afghanistan
March 31, 1952

The country of Afghanistan is situated between India and Iran and is just south of the Russian border. It is wild, rugged, and barren in many places; however, the high mountains which make up most of the geography are very beautiful with their snow caps and coloration. Like our neighbor, Tibet, we are surrounded by mountains, and Kabul can only be reached by narrow mountain passes. To come from Peshawar in Pakistan, which is the end of the railroad line, requires going over first the Khyber Pass and then the Labadan Pass. The Khyber is protected from marauding Afridi or Waziri tribesmen by garrisoned forts on each side of the road. Such picturesque forts like Koola-la-pushta and Bali-hissar (where the English were massacred) are also on the hills around Kabul. Tribesmen throughout the hills and mountains carry rifles and double bandoliers of bullets to protect themselves in the intertribal feuds. The Afghans are by nature a clever, resourceful people, and in spite of their impoverished environment a number of them are brilliant in physics and chemistry. The Minister of Education is himself a Ph.D. biochemist from the University of California, and his Vice-Minister is a Ph.D. physicist. Dr. Abu Backer at the Faculty of Science here in Kabul is doing spectrographic analysis for ozone traces in the atmosphere.

Habibia College is a government school training Afghan students in general education through the 12th grade. Since the European curriculum is employed, all students are required to study chemistry and physics in the classes from the 7th grade through the 12th grade. I teach the students chemistry and physics in the 10th, 11th, and 12th grades. In the 10th grade the curriculum covers mechanics, heat, and sound in physics, and in chemistry it covers the nonmetals and the laws of chemistry. In the 11th grade we teach light and electricity in physics and organic chemistry and metals in chemistry. In the 12th grade we review all material again which was covered in the 10th and 11th grade and in addition present new material (for example, in Chemistry 12 we present introductory quantitative analysis, certain physical chemistry subjects, and the metals of the transition groups with emphasis on oxidation-reduction reactions). Last year we undertook to teach two simple preparations in organic chemistry involving basic techniques such as steam distillation, melting points, etc., in the laboratory.

Concerning the students, many of them come from mud-walled hovels or from filthy tenements made of mud and straw and overrun with rats, scorpions, and even cobras. Malaria takes a bad toll of the students here, so it is difficult for the boys to study well in their homes. In spite of this the students are cheerful and anxious to learn.

# DRAFTED CHEMISTS AND CHEMICAL ENGINEERS AT THE ARMY CHEMICAL CENTER

**DUNCAN MACRAE**
Army Chemical Center, Maryland

LIFE as a private, private first class, or even a corporal in the United States Army will probably never be popular with drafted college graduates, but a group of chemical engineers assigned to duty at the Army Chemical Center have done much to make their off-duty hours pleasant and profitable both for themselves and others.

By December, 1951, there were about 700 draftees assigned to technical duties at the Army Chemical Center under the Army's Scientific and Professional Personnel Program.[1] Two of them—Cpl. John M. Ward, a graduate of the University of Delaware and Pfc. Kenneth L. Vander Voort, a graduate of Purdue University—conceived the idea of forming a Chemical Engineering Club with the hope that it would eventually become a local section of the American Institute of Chemical Engineers. In reply to a request for advice, Thomas H. Chilton, President of the A. I. Ch. E., wrote them a letter encouraging their idea and sent copies of it to Professor H. F. Johnstone of the University of Illinois and Dr. A. P. Colburn, Provost of the University of Delaware, both members of the A. I. Ch. E. They brought the matter to the attention of the Commanding General of the Army Chemical Center, Brigadier General William M. Creasy (also a member). He approved the plan and has since taken a personal interest in the group.

At the first meeting of the Club on March 12, 1952, Cpl. Ward and Pfc. Vander Voort were elected Chairman and Co-Chairman, respectively, and Pfc. William A. Meyer, Jr. (Johns Hopkins University), was elected secretary. The following Executive Committee was appointed: Pfc. Paul F. Oreffice (Purdue), Pfc. Lawrence C. Bartlett (Iowa), Cpl. James P. Kelleher (Newark College of Engineering), Pfc. Walter J. Ludlow (Cincinnati), Pfc. Vance B. Brown (Purdue), Pfc. Peter J. Comerford (Rensselaer), and Pfc. James H. Fisher (Georgia I. T.). Chairmen of other committees were: Program, Pfc. Joseph B. Durra (Rose P. I.); Publicity, Pfc. William F. Heneghan (Columbia); Membership, Pfc. Philip J. Ripepi (Pittsburgh).

At subsequent meetings there have been talks by the following: Thomas H. Chilton, "Why is an engineering society?"; Sidney D. Kirkpatrick, "Professional progress and problems"; Glenn T. Seaborg, "The transuranium elements." All interested persons at the Army Chemical Center were invited to attend these lectures. However, in September, 1952, there were about 1000 enlisted specialists at the Army Chemical Center and at the last meeting an audience of 600 of them filled all seats and standing room in the largest auditorium available at the Army Chemical Center.

In addition to providing a series of lectures of general interest to scientists and engineers, the Club has organized a placement service to aid in returning its members to civilian occupations promptly on the expiration of their term of active duty. A committee was formed on April 24, 1952, with Pfc. James H. Fisher as Chairman, to operate the placement service. By the end of September, representatives of 60 governmental and industrial organizations had interviewed prospective employees at the Army Chemical Center. An equal number of smaller companies had sent literature and application forms for distribution to the group. The service was open to all enlisted scientists and engineers and was used by nearly all of the 200 or more returning to civilian life between August 31 and December 31, 1952.

In establishing this placement service, the members of the club not only promoted their own interests, but also anticipated a much more general need. Since the service was begun at the Army Chemical Center, similar organizations have been established at ten other Army Posts. General Creasy has received many letters complimenting the Chemical Center and the enlisted specialists on the operation of the service and calling attention to its great value to industry during the present shortage of qualified technical employees.

It has been of similar value to the government. Approximately 35 soldiers now on active duty in the Laboratories of the Chemical Corps at the Army Chemical Center have decided to stay on in the same location after their discharge. All of the enlisted specialists at the Army Chemical Center, who are doing satisfactory work, have been encouraged to apply for similar positions as civilians. It has been gratifying to the Chemical Corps to see that many of its soldier-scientists have decided that the Corps offers them an excellent future.

The present officers of the Club are: Pfc. Eric W. Kjellmark, Jr. (Cornell), Chairman; Pfc. Floyd K. Swope, Jr. (Case), Vice-Chairman; and Paul A. F. Mourier-Peterson (M. I. T.), Secretary-Treasurer. New members of the Executive Committee include: Pfc. John J. Schrock (Pittsburgh), Chairman Placement Committee; Pfc. Delbert Cunningham (Colorado); Pfc. William A. Spartin (Illinois); Pfc. Donn R. Hoer-

[1] See "Potomac Postscripts" *Chem. Eng. News*, **30**, 1710 (April 28, 1952), and Department of the Army Special Regulation 615-25-11.

auf (Michigan); Sgt. William Prewitt (Michigan State); Pfc. Robert J. Frey, Jr. (Detroit), Chairman Membership Committee; Pfc. Gabriel Alexander (Tufts); Pfc. Norman L. Perry (Cooper Union), Chairman Publicity Committee.

The Club plans to continue its series of lectures. On October 21st its placement service began a new three-months series of appointments for employers to interview those to be discharged between January 1 and May 1, 1953.

The members of the Club are naturally much interested in the scientific manpower situation as it effects them now and as it will affect them during the next few years. They have good reason to keep up with the latest changes in the laws and regulations which affect young scientists and engineers. We believe that when they return to civil life throughout the country they will have some valuable ideas to contribute to discussions of the proper utilization of our national resources in scientific manpower.

## A NOTE ON THE ENTROPY OF A SYSTEM UNDERGOING IRREVERSIBLE PROCESSES

**MILTON KERKER**
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A NUMBER of textbooks of chemical thermodynamics [1–3] treat the entropy change experienced by an isolated system undergoing irreversible processes. The purpose of such treatments is to show that

$$dS_{\text{system}} > 0 \tag{1}$$

The first step is to state that for any process

$$dS \geqq \frac{DQ}{T} \tag{2}$$

where the equality pertains to a reversible process and the inequality to an irreversible process. This statement can be derived from one of the enunciations of the Second Law or it may be stated axiomatically as the Second Law.

The isolated system is then divided into a medium and surroundings. Each infinitesimal step of the process is characterized by a transfer of heat from the surroundings to the medium which undergoes an irreversible process. Let the heat absorbed by the medium be $DQ$ and that absorbed by the surroundings be $-DQ$. The usual formulation states that

$$dS_{\text{medium}} > \frac{DQ}{T} \tag{3}$$

$$dS_{\text{surr.}} = -\frac{DQ}{T} \tag{4}$$

so that

$$dS_{\text{system}} = dS_{\text{medium}} + dS_{\text{surr.}} > \frac{DQ}{T} - \frac{DQ}{T} > 0 \tag{5}$$

Equation (4) requires that the surroundings themselves undergo a reversible process. This point is often a source of confusion to many students who feel that it implies that the surroundings must *necessarily* change reversibly in order that the proof be successful. They feel that the medium and surroundings are inseparably involved in the same process and the restriction of the surroundings to reversible changes strikes them as being artificial. It is unnecessary to make this restriction and the treatment is actually more general and natural if the surroundings are also permitted to change irreversibly. In such a case

$$dS_{\text{medium}} > \frac{DQ}{T} \tag{3}$$

$$dS_{\text{surr.}} > -\frac{DQ}{T} \tag{4a}$$

and

$$dS_{\text{system}} = dS_{\text{medium}} + dS_{\text{surr.}} > \frac{DQ}{T} - \frac{DQ}{T} > 0 \tag{5}$$

If there is a temperature difference between the system and surroundings,

$$dS_{\text{system}} > \frac{DQ}{T_{\text{medium}}} - \frac{DQ}{T_{\text{surr}}} = DQ\left[\frac{T_{\text{surr}} - T_{\text{med.}}}{T_{\text{surr}} \times T_{\text{med.}}}\right] > 0 \tag{6}$$

since $DQ > 0$ when $T_{\text{surr.}} > T_{\text{medium}}$, and $DQ < 0$ when $T_{\text{surr.}} < T_{\text{medium}}$.

[1] KLOTZ, I. M., "Chemical Thermodynamics," Prentice-Hall, Inc., New York, 1950, pp. 96–7.
[2] GLASSTONE, SAMUEL, "Thermodynamics for Chemists," D. Van Nostrand Co., Inc., New York, 1947, pp. 144–6.
[3] STEINER, L. E., "Introduction to Chemical Thermodynamics," 2nd ed., McGraw-Hill Book Co., Inc., New York, 1948, p. 164.

*Report of the*

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

# THE FIRST FIFTY YEARS ARE THE HARDEST[1]

**AUGUSTUS KLOCK**
Fieldston School, New York, New York

My remarks will be largely in the spirit of reminiscence, somewhat after the manner of that delightful book, "And Gladly Teach," by Bliss Perry. They will, however, also have implications for the future.

What I should like to present is a species of very short autobiography where the first person singular will be soft-pedaled and where my impressions of personalities, publications, places, and institutions during my fifty years of teaching will be stressed. Most of these personalities and institutions were involved in the history of the New England Association of Chemistry Teachers and, thus, were a part of your life as well as of mine. Brief reference, also, will be made to a philosophy of life and a philosophy of teaching which also distilled out of contacts with young people in my laboratory and my classroom.

But perhaps most important will be the appreciation of persons and institutions which have made my teaching span a veritable heaven on earth during these fifty years.

The title of this paper means, when translated, that in June of this year I completed fifty years of chemistry teaching. There is nothing particularly remarkable about that, except that these fifty years have been the greatest, in terms of the development of chemistry, that the scientific world has ever seen.

It is my deep conviction that as we do honor to the people who, by their lives and their works, have enriched our lives and that of our Association, we do honor to ourselves. One of the ways of achieving this is by articulate appreciation of what they have meant to us.

One of the first to be mentioned under this heading is *Dr. James F. Norris* of Massachusetts Institute of Technology, "Sunny Jim" to us who knew him well. It was my privilege to be secretary of this Association during the two years, 1907–09, when he was president. His leadership, his devotion to the Association, his capacity for fellowship, his genial nature, his fine sense of humor and his ability made everyone who knew him love and respect him. During this same span of years and afterward I had the privilege of being reader in chemistry for the College Entrance Examination Board when Dr. Norris was not only head examiner in chemistry but also head reader. In that era the College Entrance Examination Board was a vital, living institution doing great service to chemistry in raising the standards of high-school chemistry teaching.

Lack of time prevents anything more than brief reference to a number of others of that period:

*Prof. Henry P. Talbot* of Massachusetts Institute of Technology, charter member of this Association, and one of its most outstanding friends for two decades.

*Prof. Charles James*, tall, modest, expert on the rare earths. I still remember vividly the array of 17-in. evaporating dishes on the lecture table, at the then New Hampshire College, containing crystals of pure rare-earth compounds which he had obtained in that degree of purity, in some cases, as a result of some 10,000 recrystallizations.

*Dr. Lyman C. Newell*, quiet, scholarly, dignified, high-school and later college teacher. Devoted member of this Association and its first president. Prolific writer of textbooks.

*Laura B. White*, outstanding chemistry teacher in the Girls High School, Boston. Hostess extraordinary. At home at Girls High School one Friday afternoon each month to chemistry teachers of Boston and vicinity.

*Wilhelm Segerblom*, devoted member of this Association and its president during 1915–16. Author, loyal and devoted friend. It is our great privilege that, after his death, his good wife has kept his spirit alive in this Association with unparalleled devotion.

*Edward F. Holden*, our last surviving charter member. Treasurer, 1899–1906. Vice-president in 1907–09 when I was secretary. Brilliant, witty, with a sharp tongue, he was not only one of the most devoted members of the Association but flavored its activities with tabasco sauce.

*Lillie C. Smith*, treasurer for many years. Of

[1] Presented at the 14th Summer Conference of the New England Association of Chemistry Teachers, University of Vermont, Burlington, Vermont, August 22, 1952.

gracious charm and friendly spirit, combined with great ability and great devotion to the Association. Left a bequest to start our Endowment Fund.

*Charles E. Dull.* Prolific writer of books, faithful and helpful attendant at our summer conferences. We very much miss his contribution to the spirit of fun, his sense of humor, and his inimitable stock of good stories.

*Frederick C. Adams* followed me as president of our Association. I want to register my gratitude for the privilege of knowing this able, devoted, and spiritually fine person.

During the period in the history of the New England Association of Chemistry Teachers from 1905 to 1910 the Association was the beneficiary of the Lowell Institute in the form of Saturday courses for teachers. Through the kindness of Dr. A. Lawrence Lowell, then president of Harvard University, our Association was able to arrange a series of free courses for teachers on Saturday mornings and other convenient times. Thus we had a course in physical chemistry by Gilbert Newton Lewis, a course in Industrial Chemistry by Frank H. Thorp, and a course in Sanitary and Food Chemistry by Ellen H. Richards—all of the Faculty of the Massachusetts Institute of Technology.

## TEXTBOOKS

Two men who, by their textbooks, profoundly influenced the teaching of chemistry in both high school and college, prior to the turn of the century and the decade or two that immediately followed, were Ira Remsen and Alexander Smith. My chemistry textbooks in high-school and freshman college were Remsen's. They were good books of their kind but they were highly descriptive and, in a factual sense, a "catalogue of ships." I still remember my thrill as a young teacher in the Beverly High School (Beverly, Massachusetts) along about 1906, when Alexander Smith's "General Chemistry" first came to my attention. Here at last the facts of Remsen's texts were invested with the "how" and the "why." At long last, chemistry had become an exalted science with its fundamental principles, both physical and chemical, forming its vertebrate structure. The energy side of chemical change was considered quite as important as the matter involved. The teaching of chemistry became more thrilling as the students responded more enthusiastically to this more satisfying physical-chemistry approach. Needless to say this has continued through the years and is one of the reasons for the joy I have got out of chemistry teaching. Needless to say also that the host of good chemistry textbooks that have appeared during the last forty years have followed the same pattern.

Nor was the physical chemistry approach the only great contribution of Alexander Smith. His use of chemical terms with precise, specific meanings clarified chemical thinking by removing the hazy, wooly, fuzzy terminology of some earlier authors and thus made concepts, previously thought to be difficult, crystal clear to the student. The fact that "difficult subjects are made easy in proportion as their wording is made clear and precise" is not however confined just to chemistry.

## HISTORICAL APPROACH

The longer I have taught the more I have felt that the historical approach is the best for the kind of students it has been my privilege to teach. At the very beginning of my course I tell the students that they are going to live through, in one short year, the evolving development of scientific chemistry that, historically took almost 200 years to achieve. Thus they get the feeling that they are part of an evolving, growing thing which, with its rich symbolism, its fundamental principles, its fascinating theories to explain these principles, becomes a romance quite as thrilling as any story book or any movie. Moreover, with the practical nature of the subject matter at every turn, coupled with the vigorous play of the imagination in using theories to explain fundamental principles, along with the preparation of new substances from original substances in the laboratory, they see that chemistry is just as creative in the chemistry course as creative writing is in the English course.

Moreover, as with these students the more complex evolves out of the less complex (even as it did through the centuries as chemical research discovered one fundamental law after another), a thread of sequence runs through our course, similar to but not identical with that which runs through a course in geometry. This gives it a kind of esthetic beauty to the young mind. Many is the student who has confessed to me after a few months of chemistry that, whereas she dreaded the chemistry course prior to entering it, she was now fascinated by it and loved chemistry. For her it was a new and thrilling realm in human thinking.

Important in this historical approach is the fact that I have collected an historical bookshelf of chemical books showing the progress of chemistry during its nearly 200 years of growth. Starting with the period of Cavendish and Lavoisier and mostly in the form of textbooks, these publications run right through the nineteenth century, and then continuing in the twentieth century end up with books of modern authors. On examining this shelf of books, students discover no symbols or formulas (as we now know them) in the books right up until about 1830. Then formulas begin to appear, but most of them are incorrect until we reach the textbooks of 1870. Thus comes home to the student the work of Berzelius who is responsible for our modern symbols; and, more important, the role of Avogadro's principle which, though enunciated in 1811, but not understood until 1858, made correct formulas impossible, except by chance, until after 1860. The fact that from 1850 to nearly 1870, in chemistry textbooks, water was HO and hydrogen peroxide was $HO_2$ drives home to the student the importance of Avogadro's principle more than pages of exposition could possibly do.

## LABORATORY

Another of the things that I have found best for *our* students in scientific courses—biology, physics, and chemistry—is the laboratory-based type of course. This means that the laboratory work (and we have a rather heavy laboratory program for a preparatory school) is done, and the report on it written, before any assignment is made on the corresponding topic in textbook or reference book. As a matter of fact, we go further than this; the student does the laboratory work, writes his report on it, and corrects it after the teacher has criticized it. Then when all of the students have reached this stage for a particular experiment a class discussion of the experiment follows in which the significance of the experiment, in and for itself and in its relation to the course and to the practical outside world, is brought out.

The theory underlying this is that the only "real" chemistry, from the student's point of view, is that which he faces in the laboratory where he doesn't know the answers beforehand. Here, of course, he has the chance to get the thrill out of discovering something; and a thrill they do get. This is one of the biggest reasons why, in a senior class of 85 in our school, 65 regularly elect chemistry (though chemistry is an elective and is in competition with other subjects in a program limited to four majors).

Now we are not trying to train Einsteins or Pasteurs or Lavoisiers (though we do often have the near equivalent of J. Robert Oppenheimer). We believe that out of the comparatively crude laboratory work which the rank and file of students do, they get something that you can't get out of a textbook. We lead them to see that the textbook is in reality the highly distilled, highly organized, highly corrected product of the laboratory work of a host of very able people who preceded them. Of course, we do not have time to do laboratory work on all of the topics of our chemistry course, but what laboratory work they do, in the manner above described, gives them a basis for understanding the origin of all textbooks and reference books with which they later came into contact.

## TESTS AND WRITTEN WORK

Another thing we have found of great educational value in our chemistry course (and also in our physics course) is our way of treating examinations. A student who takes an examination (final, midyear, monthly, or even a five-minute test) is not only given his grade on the test but is given his examination book or paper as well. Since the examination paper has been *criticized* in red pencil like any other piece of chemistry manuscript, in the process of *rating* it, the student now has to *correct* his examination. Thus he meets head-on and corrects all his errors of fact, misspelling, and omission and, in a later conference with the teacher, must get his exam O.K.'d. We have found this procedure to have great educational value, and *mystery* is incidentally taken out of examinations.

A word about the five-minute test just referred to may be in order. This is a short test, given precisely at the beginning of the period, on any topic from laboratory work, textbook, or general class discussion, of the work previously studied. Its nature varies all the way from a memory question to a power question. We have found it a most stimulating device to keep students on their tiptoes and to encourage prompt arrival to class of pupils of dilatory natures.

Now for our attitude toward *written work*, such as laboratory reports, special reports, and examinations: we feel that the teaching of English should not be confined to the classroom of the English teacher, that it is just as much the duty of the chemistry teacher to insist that the student strive to express himself in clear, precise, logical English in the chemistry course as for the English teacher in the English course. Clear thinking, we believe, goes along with clear, concise, English expression both orally and in writing. Moreover, this helps to avoid both vague, fuzzy thinking on the part of the student and also what we often call "engineering English."

And so we have evolved a sheet of symbols used in our criticism of written work which is given to every student and which he must utilize in the correction of his written work. Since lack of space precludes the publication of this list here, it should be said that in preparing the list we were not concerned merely with things like misspelling, but rather with such things as lack of logical thinking and insensitivity to the scientific method.

## COLLEGE ENTRANCE EXAMINATIONS

I now come to the only black cloud hanging over the chemistry teaching of my fifty years. I refer to the changed role of the College Entrance Examination Board and to the change not only in the *character* of its chemistry examination but also in the *procedure* by which that examination is administered. In order fully to understand this new era of the Board, it is necessary to know the background of the Board's history

The College Entrance Examination Board had its inception in 1902 at the very beginning of my teaching career. For nearly forty years, largely under the guidance of its secretary, Prof. Thomas S. Fiske of Columbia University, it was not merely a superb device for determining the proficiency of college candidates; it was a great educational institution as well. Indeed, it was a vital, living organization doing great service to chemistry in raising the standards of high-school chemistry teaching.

A group of high-school and college teachers, called examiners, carefully prepared its examinations. A much larger group of high-school and college teachers, called the board of Revision, carefully criticized the examination as prepared. Thus the examination questions were validated in extreme fairness both to the high-school candidates and to the standards of

college teachers. *Moreover, the examination came in June at the end of the student's course* and at that time proved not only an excellent test of the fitness of the high-school student but a welcome challenge to the high-school chemistry teacher as well. And most important of all, the examination coming at that time made it possible for the chemistry teacher to give his course with hardly a thought, during the year, of the chemistry examination.

Immediately after the examinations were taken in June, the examination blue-books were read and rated by another group of high-school and college teachers from all over the country. This group, called the board of readers, not only employed great fairness in appraising the examinations but learned tremendously from one another in doing so.

Having shared in the work of these various committees and boards during many years, I can attest to the supreme fairness of their action and the high educational value to both high-school and college teachers of thus working together. This was a fine democratic setup which not only resulted in fairness to the examination candidate but in the high-school teacher's learning the college point of view and the college teacher's understanding the high-school student.

It must be remembered, also, that in those days the Board issued an *official, detailed syllabus*, open to all, worked out again by a committee of high-school and college teachers showing in detail the chemistry content on which the examination was based.

About 1940, with the retirement of Prof. Fiske, the Board took on new management—a group of statisticians, who reorganized the board on a machine basis. First of all they placed the whole examination setup behind the iron curtain. Then they discarded onto the scrap heap, to a large extent, the subjective human side of examination procedure, substituting for it the machine. Then, worst of all, they became *the tool of the admissions offices of the colleges* and placed the chemistry examination early in April, right in the midst of the high-school course, instead of in June, at the conclusion of the chemistry course. A year or so later, as if the lunacy of the April examination were not enough, they moved the examination back to early March. (I suggest that still better in accordance with their practice would be to give the examination in September at the beginning of the course and "get it out of the way.")

Remember also that there is now no official syllabus of topics, basic to the examination, accepted by the Board. That excellent syllabus arrived at by a committee of this Association a couple of years ago is thought of as the Board syllabus by some people but, so far as I know, has never been officially accepted by the Board. Even then, how much of it should be covered by early March?

As a sample of what we are up against let me remind you of the chemistry examination which our students took last March. The examination candidate began his examinations at nine o'clock in the morning of the Saturday given over to C.E.E.B. exams. Around three o'clock in the afternoon, after a grueling day of exams that began with English, he was given his chemistry test. This exam last March contained 160 questions to be done in 60 minutes by a student already fatigued by previous examinations. Is this fair or even sane, I ask?

The disservice to chemistry teaching in the senior year of the high school, thus done by the present C.E.E.B. procedure, is nothing short of tragic. In the first place the kind of examination that can be marked by a machine is greatly inferior to the more subjective type of examination which the board gave for almost forty years. It caters to the non-laboratory cram type of chemistry course and penalizes the better type of chemistry course that seeks to develop the power to think in chemistry—and the power to organize that thinking sequentially and effectively. In fact, coupled with the time at which the examination is given, it is a factor so demoralizing to senior chemistry courses that it now takes the heart out of teaching these courses. Indeed it menaces the future of these courses. Moreover, you can't blame an average student for feeling after a college board exam in early March that somehow the chemistry course is over. It is a natural psychological reaction which only the best chemistry teachers can completely offset and then, for the most part, only with their best students.

Keep in mind that statisticians aren't bad people; they are practical people who sometimes ignore the psychological and educational side of human activity in their quest for a goal. If they could discover a chemical indicator which could measure the proficiency in chemistry of college entrance candidates, they would use it. Obviously then they are not primarily interested in education. Since, however, they are the agents of the admissions offices of the colleges, the colleges are primarily to blame.

Moreover the personalities who prepare the modern C.E.E.B. chemistry exam, many of whom are from this Association, are able people fulfilling the wishes of the Board's administrators. It is not they but the system that is wrong.

It is in one-year senior subjects, like chemistry and American history, that the situation is serious; courses in English, mathematics, and languages begin at least three years before the senior year and so an exam in March is much nearer the end of the course than in a one-year senior course. Moreover, knowing the thrill that students get from a well-integrated *chemistry* course, which must be true in a host of schools, I want to go on record as saying that a hodge-podge of biology, physics, and chemistry, lasting several years and merged into a single examination, is no solution. Well what is the solution of this tragic problem?

My teaching days are largely over, but I am keenly anxious nevertheless about the future. And so consider this heartfelt but respectful diatribe of mine as an expression of desire on my part that all the parties

involved in this situation should strive for a solution. And that right soon!

**FINAL REFLECTIONS**

I have often been asked for reflections on teaching and teachers. I here mention only a few:

Teaching has great therapeutic value; teachers are so engrossed in the manifold duties of working with young people that they forget their other troubles and live the longer for it. The only trouble is that when you are very busy teaching, the years pass so quickly you are seventy before you know it.

Teachers have to care for young people to enjoy their work; and when they do they become a part of the life of the student while he is in school and live on in the lives of their students even after graduation—even after the teacher has retired.

One of the most important components of the personality of a teacher is a sense of humor; it is the catalyst in life's reactions.

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I want, in conclusion, to express my appreciation of what Harvard, my *alma mater*, and the New England Association of Chemistry Teachers have meant to me during my fifty years of teaching. Not having been a native of New England, I can all the more decorously sing the praises of both institutions.

Two of Harvard's great presidents, Eliot and Conant, came by way of chemistry. One of its early professors, Josiah P. Cooke, the "Father" of laboratory chemistry, was by his writings an inspiration to me as a young teacher. To one of Harvard's graduates and, latterly, one of its professors, N. Henry Black (teacher of President Conant), I am indebted more than words can tell for his writings, his friendship, and his colleagueship steadily during almost fifty years.

One of the great contributions to laboratory chemistry, inspired by Prof. Cooke and given by Harvard, was the laboratory examination in chemistry required of all entrance candidates offering chemistry for admission. This examination given in the Harvard laboratories (Boylston Chemical Laboratory) was in addition to the written examination (Harvard or C.E.E.B.) and was a great boon to good chemistry teaching. It was a tragic loss to chemistry when in later years this examination was discontinued by Harvard.

From its very earliest years the New England Association of Chemistry Teachers has set the pattern for the best in chemistry teaching. The caliber of its meetings and the fellowship of its members have been outstanding during the years. Morever, its week-long chemistry conference each summer, the first of its kind in America, has for 14 years been a mecca of inspiration, fellowship, and instruction, not only for New England teachers of chemistry but for hosts of teachers outside New England.

To all of the above institutions and personalities (and a host of unnamed others) I give my thanks, inadequate but heartfelt, for what they meant to me.

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*To the Editor:*

Recently I accidentally came across a reference to a relationship between atomic weight and atomic number which was claimed to be an improvement over a previous relationship. The new relationship, found by I. R. Morozov (*Zhur. Obshcheĭ Khim.*, **20**, 555 (1950); *Chem. Abstracts* **44**, 6208*g*), was $A = (2 + Z)^{1.2}$, an improvement over Vincent's equation, $A = Z^{1.21}$.

For years, whenever caught without a table of atomic weights, I have calculated atomic weights from atomic numbers by a linear interpolation of the ratio $A/Z$ between $A/Z = 2.0$ at $Z = 2$ and $A/Z = 2.6$ at $Z = 92$. These numbers are easily remembered, or can be calculated from the atomic weights and atomic numbers of helium and uranium, which are also easy to remember. The arithmetic is much simpler than in the case of either Morozov's or Vincent's relationships. The error in atomic weight is usually no greater than one unit or so. The equation corresponding to this interpolation is $A = Z\,(2 + 0.0065Z)$.

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# Film Reviews

## • COLLOIDS

*Description:* 16 mm., sound, 10 min.

*Producer:* Encyclopedia Britannica

*Reviewers:* (A) R. C. White, North Carolina State College of Agriculture and Engineering, University of North Carolina
(B) L. H. Reyerson, Institute of Technology, University of Minnesota
(C) R. T. Schenck, New York University

*Possible Utility:* (A) "It is suitable for courses, such as general chemistry, physical chemistry, and biochemistry, in which a short time only is devoted to colloid chemistry. The film is not adequate for a course in colloid chemistry, except for stimulating interest and giving a survey at the beginning of the course." (B) "This film should be useful for beginning students in chemistry and possible for Premedical students taking Physical Chemistry."

*Film Content* (from (A) and (C)): The film shows how the colloidal state is intermediate between a coarse suspension and a true solution. When sand is mixed with water, the particles settle out, leaving a clear supernatant liquid. Clay mixed with water is shown to separate only partially, leaving a milky suspension which passes through filter paper. The Tyndall effect is shown by colloidal gold in water, but not by a true solution, nor by the suspension of clay which is too opaque. The Brownian movement is photographed, and explained by animated drawings. Examples of different types of colloidal systems are shown, such as fog, whipped cream, India ink, and smoke. Stable and unstable colloidal systems are depicted. Stabilization by protective coatings is explained, and illustrated by mayonnaise and silver chloride precipitated in the presence of gelatin. The action of soap is illustrated. Stabilization through the adsorption of ions is shown by animated drawings. The electrical properties of colloidal systems are then shown, including migration of clay particles in an electric field and coagulation of suspended particles through charge neutralization, including the precipitation of smoke particles by a Cottrell precipitator.

*General Criticism and Rating:* (A) "The content of the film is accurate and worth while." (B) "Except for some lack of continuity, probably to be expected in an eleven minute film, the material as presented seems quite clear and informative. Perhaps the film is most useful in emphasizing the fact that matter may exist in several degrees of subdivision, one of which is the colloidal state. However, the film fails to delineate precisely this state as to dimensions." (C) "Only fair. Demonstrations not too successful because by their nature they are seldom clear-cut (for instance, AgCl does not coagulate completely, and the curds at the bottom are nearly invisible under the still-milky supernatant.) You can't tell by watching a kitchen mixer work how mayonnaise is forming in the bottom of the bowl, or from the outside of a colloid mill what's going on inside."

*Suggestions for Improvement:* (B) "The film we saw was not in good shape and should be rerun." (C) "This would be greatly improved by replacing most of the photography by animation, to show things like orientation of surfactants in oil-in-water and water-in-oil emulsions, etc."

## • IRON AND STEEL

*Description:* 16 mm., sound, 10 min.

*Producer:* Films, Inc.

*Reviewers:* (A) Edwin M. Larsen, University of Wisconsin
(B) Warren H. Yudkin, Northwestern University

*Possible Utility:* (A) "The film is not recommended for freshmen college classes." (B) "As it now stands, however, it is to be recommended as possibly worth while to be shown in a rapid, superficial survey course. Engineers will be interested in this film because of the protracted section given to milling and pressing operations."

This film would probably be of general interest in showing the production of iron and steel from a very nontechnical viewpoint.

*Film Content* (from (A) and (B)): The production of iron and steel from the open-pit mine to the final finishing of steel rails is presented in this film. It shows briefly the mining operations in Minnesota, and the loading of the ore onto ships which carry it to mills on the Great Lakes. Exterior pictures of the blast furnaces and coke ovens are shown and then animated sketches showing the loading of the blast furnace and its operation. The mechanical operations of the blast furnace are quite clearly illustrated. The formation and separation of slag are clearly shown, as are the actual tapping of the blast furnace, the pouring of the molten iron into molds and ladles. The Bessemer converter and the open-hearth furnace in operation are depicted by actual photgraphs as well as animated sketches. The air-duct system of the open-hearth furnace is explained in diagram. Finally, the pressing and milling of steel into its various forms, notably rails, are given a great deal of attention.

*General Criticism and Rating:* (A) "There is no question about the authenticity of the production, but so little chemistry is discussed that it does not seem worth while . . . the quality of the photography is poor." (B) "This film suffers from a dearth of chemistry. Nowhere are any operations either in smelting or refining described in chemical terms. Limestone is mentioned, for instance, as being added to purify the iron but its role in the formation of slag is hardly emphasized. The spectacle of the Bessemer converted in action is shown but a diagram illustrating its operation would have well served to bring forward the slighted subject of the elements of the conversion of iron to steel. Scrap metal is illustrated brought to the steel mill but the specific reasons for the addition of the scrap are omitted."

*Suggestions for Improvement:* (A) "The sequence of events and choice of topics are good, and if they were developed more extensively as far as the chemistry is concerned, the result could be a production satisfactory for freshman college courses." (B) ". . . this film if reinforced with some chemistry might aid in teaching the subject of iron and steel production in an elementary course in general chemistry."

## ● THE PHASE RULE AND ITS APPLICATIONS

**_Alexander Findlay_, Professor of Chemistry, University of Aberdeen. Revised by _A. N. Campbell_, Professor of Chemistry, the University of Manitoba and _N. O. Smith_, Associate Professor of Physical Chemistry, Fordham University. Dover Publications, Inc., New York, 1951. xii + 494 pp. 236 figs. 57 tables. 14 × 20 cm. $1.90.**

It is probably an easier task to write an acceptable text on a broad subject, encompassing a whole field, than to write a book dealing with a restricted portion of a technical field. The potential customer, examining the offering of the specialized authors, will note, if it is indeed a good book, that there is a wealth of detail on matters that are of minor concern to him; and this same critic will quickly observe that his own particular interests have been treated lightly.

This book does not cover, in any detail, the applications of the phase rule to problems in mineralogy, geology, and ceramics. The outstanding omission, however, is the lack of emphasis on thermodynamics. To be sure, this tool is used, particularly in Appendix I, which treats of the graphical thermodynamic deduction of temperature-composition diagrams. However, the thermodynamic treatment is not used as much as it could have been in other sections. For example, the derivation of the phase rule follows the semi-quantitative, arithemetical method frequently found in elementary physical chemistry texts. A reference is cited to a more sophisticated, Gibbsian derivation.

The authors claim, correctly, that this edition has been largely rewritten. A rough check indicated that approximately 75 per cent of the material, counted by pages, was wholly or partially revised, including new additions. New material on binary and ternary liquid-vapor equilibria, solid solutions in ternary systems, and phase changes occurring in the cooling of ternary melts has been added. The treatment of quaternary systems of salts and water, critical phenomena in binary systems, salting-out, soap systems, fuming liquids, and the free-energy basis of binary and ternary condensed systems is also new. But in a few instances the authors stopped short of the desirable point in their revisions. For example, on page 208 we find: "The study of the formation of minerals...is now attracting considerable attention[37]...." Item 37 lists 19 references, the most recent one dated 1935. This quoted sentence was taken from the previous edition (1938), at which time the fact that work was currently being conducted was substantiated by the references cited.

The general impression gained upon examination of this book is that this new edition was well conceived, executed well initially, but that in the last pangs of birth too much haste was made.

To cite the many fine features of this book with as much detail as has been used in considering the few weaknesses would make this review too lengthy.

This book is well organized. After a two-chapter introduction, systems of one component are discussed, two chapters; then two-component systems, eight chapters; then three-component systems, six chapters; and finally two chapters are devoted to four, five and six-component systems. There are two appendixes, one discussed above; the second appendix describes the experimental determination of binary solid-liquid equilibria.

The authors make liberal use of examples from the literature in discussing each subordinate topic In a sense, this book would make an admirable reference for the inorganic chemist because of this feature alone.

However, the most favorable feature of the book, only slightly dimmed by the use of a poor type face, is the fact that the book is technically correct, readable, and interesting. No graduate student or professional man in chemistry, physics, or metallurgy, worthy of his title, can fail to be interested in this book. Almost every sentence is loaded with food for studious meditation and the reading pace is therefore slow. But the style is sufficiently interesting to induce the reader to turn the page, see what comes next, and therefore almost without any unpleasant effort learn about the wonderful implications of $F = C - P + 2$.

The copy received for review was paper-bound, thereby, according to the publisher, lowering the cost to approximately 40 per cent of the also available cloth-bound edition. Both editions are identical in content. The low-cost binding is similar to, but somewhat better than the binding used on the popular pocket-book reprints available almost everywhere. With care, the paper-bound edition would probably stand nine or ten months of textbook use. There is certainly a definite need for good low cost technical text books. The publisher is to be commended for his partly successful efforts in this regard.

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## ● A SOURCE BOOK IN CHEMISTRY: 1400–1900

**_Henry M. Leicester_, College of Physicians and Surgeons of San Francisco, and _Herbert S. Klickstein_, Edgar Fahs Smith Library in the History of Chemistry, University of Pennsylvania. McGraw-Hill Book Co., Inc., New York, 1952. xvi + 554 pp. Illustrated. 15.5 × 23.5 cm. $7.50.**

This compilation of 123 significant publications or parts of publications written by 82 famous men is a recent addition to a notable series called, "Source Books in the History of the Sciences." Chemists who are interested in the past records of their own field should welcome it, for there is a wealth of well-selected original material which contributed to the advancement in chemical theory. These writings are those which are generally considered most influential for contemporary thought and subsequent development of chemistry. Yet they are not necessarily the first to be printed on the subject. English translations, where needed, are those made near to the time the material was first published in order to emphasize the meaning which the material had when it was first recognized. The first two excerpts were by Biringuccio and Agricola, and the last three by Gomberg, Werner, and Madam Curie, conclude this extensive collection from the works of many distinguished investigators.

Each selection is introduced by a few paragraphs written by the compilers, which include the dates of the author's life, the ideas which lead up to his contribution, and additional significant conceptions for which the author is famous. Not only is the exact reference for the selection given but also occasional references to reprints which might be more accessible to the reader. The lack of biographical information is owing to lack of space. There is, however, a bibliography of biographies at the end of the book to enable the reader to learn more about these personalities who have a permanent place in the history of chemistry.

To a teacher of the history of chemistry, this book will be of enormous value and great benefit. For the undergraduate courses it is a long-needed reference book because this source material has been for the most part either scattered or not readily available in English. There is nothing comparable to the stimulus which students receive when they read the original records of famous men which show the steps by which they reached their conclusions

from experimental evidence. The volume is informative, good training in logic, presents examples to emulate, and indicates the mobility of thought required in a science. For small or selected classes with a close relationship between instructor and student or for the seminar type of presentation, this book would be excellent and adequate for a text. The chronological arrangement shows the trend in theoretical chemical thought in such a way as to be fascinating for any chemist.

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## • MODERN CHEMICAL PROCESSES. VOLUME II

**By the *Editors of Industrial and Engineering Chemistry* and technical staffs of cooperating organizations. Reinhold Publishing Corp., New York, 1952. v + 299 pp. Illustrated. 21 × 29 cm. $5.00.**

SINCE February, 1948, one of the editors of *Industrial and Engineering Chemistry* has cooperated with the technical staff of an industrial organization to describe comprehensively a new plant or process, replete with excellent illustrations and flowsheets. In Volume I of this series were collected the 23 articles appearing in 1948 and 1949. In Volume II are the 24 articles appearing in 1950 and 1951. Of these, six describe inorganic processes and 18 describe organic processes (of which four are biochemical processes). The processes range from "reagent grade chemicals" through "pioneer surfactant" to "brewing" and "modern wine-making." Some articles, like "calcium cyanamide," represent the first authoritative description given of an older industry and its modernization. Others, like "magnesia-base sulfite pulping," are the first complete technical description of a new process seeking to revolutionize the industry. Because of the close cooperation between the editorial representative and the company representatives the articles are always well written, well illustrated and authoritative.

The articles in the book are not arranged in the sequence in which they appeared in *Industrial and Engineering Chemistry*. It would be helpful to have beneath the title the *I.E.C.* reference for those who wish to quote the reference.

"Modern Chemical Processes" will save much wear and tear on *I.E.C.* and for itself merits a place among the texts on chemical technology.

KENNETH A. KOBE

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## • UNIT PROCESSES IN ORGANIC SYNTHESIS

**P. H. Groggins, Editor-in-Chief, Chemical Engineer, U. S. Department of Agriculture. Fourth Edition. McGraw-Hill Book Co., Inc., New York, 1952. xiii + 937 pp. Illustrated. 15 × 23 cm. $12.50.**

THE appearance of a fourth edition of this book only five years after the third edition attests to both the importance of developments in the field and the utility of the book in presenting the unit process phase of chemical engineering as applied in the organic process industries.

The unit processes discussed are those of the third edition: nitration, amination by reduction, diazotization and coupling, halogenation, sulfonation, amination by ammonolysis, oxidation, hydrogenation, esterification, hydrolysis, polymerization, alkylation, Friedel-Crafts reaction. To these has been added a new chapter on hydroformylation: The Oxo Reaction by M. Orchin and W. C. Schroeder of the U. S. Bureau of Mines.

For a typical chapter, major subdivisions for Nitration are: definition, survey of nitro compounds, examination of nitrating agents, kinetics of nitration, thermodynamics of nitrations, equipment for nitrations, technical nitrations—nitrobenzene, *m*-dinitrobenzene, chloronitrobenzene, p-nitro-acetanilide, mononitrotoluenes, alpha-nitronaphthalene, nitroparaffins, recovery of spent acid from nitrations, and the economics of nitration. Although nitration is defined as a process for introducing $—NO_2$ or $—ONO_2$ groups into organic compounds, the production of glyceryl trinitrate and cellulose nitrate is discussed in the chapter on esterification.

The significant changes between the third and fourth editions, other than reference to most of the recent work, are the inclusion in each chapter of sections on kinetics, thermodynamics, and economics of the unit process. Frequently these subsections are written by men who have had particular experience in those fields. This changing emphasis on the unit processes and combination of thermodynamics, kinetics, and economics with the study of unit process variables and equipment design is most important and will help to put the unit processes on a quantitative basis.

The fourth edition will continue to serve as a text in unit process courses. It will find even greater acceptance among teachers of organic chemistry who will refer their students to it to learn how the organic reaction discussed in class and conducted as a laboratory preparation is translated to a tonnage basis by industry and what new problems are involved in this scale-up of the process.

KENNETH A. KOBE

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## • NOMOGRAPHY AND EMPIRICAL EQUATIONS

***Lee H. Johnson*, Dean of the College of Engineering, Tulane University. John Wylie & Sons, Inc., New York, 1952. ix + 150 pp. 92 figs. 18 tables. 15 × 23 cm. $3.75.**

THIS is a short, easy-to-read, well-written cookbook on the construction of nomographs and the fitting of empirical equations. In both the presentation of his material and his attitude towards experimental data, Dean Johnson has followed Lipka's "Graphical and Mechanical Computations" (Wylie & Sons, Inc., 1918). He has modernized the problems and Wylie has improved the typography, but—except for considerable omissions—this book can be considered a revision of Lipka. Engineers who need detailed advice on the construction of the commoner forms of nomographs will find it useful. The usual formulas for moments of inertia and the discharge from weirs make their inevitable appearance and are duly provided with appropriate charts.

But a lot of water has gone over those weirs since 1918, and the rational for least-squares-fitting of their data has been extensively studied. Probabilistic approaches have given simple, powerful methods which should not be ignored, even in an elementary exposition. Not only will such techniques extract more information from the data, but their use will lead the engineer to examine the structure of both his theory and experimental errors —a desirable change from the here-are-the-numbers-let's-fit-'em philosophy of the last generation. This reviewer feels that it is important to discuss *why* we fit data, as well as *how* we fit them. It takes more space, but to remove the fitting problem from its context, renders adequate advice rather difficult.

In order to keep his treatment brief, Dean Johnson has omitted all discussion of periodic curves. He further restricts his exposition to the mathematical machinery of simple algebra, similar triangles, and common logarithms. (For instance, the Napierian base, $e$, is never mentioned. Equations of the form $y = ae^x$ are fitted as $y = A(10)^x$.)

He does not present the *mathematical* art of nomography, nor does he pretend to. These limitations in scope, machinery, and viewpoint bar this book as a good college text, but its numerous problems are happy additions to the instructor's reservoir.

FORMAN S. ACTON

NATIONAL BUREAU OF STANDARDS
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## ● LABORATORY MANUAL FOR FIRST YEAR COLLEGE CHEMISTRY

*John W. Barker,* Professor of Chemistry, Wittenberg College, and *Paul K. Glasoe,* Professor of Chemistry, Carthage College. McGraw-Hill Book Co., Inc., New York, 1951. xi + 186 pp. 21.5 × 28 cm. $3.

"This laboratory manual is designed to provide a full year of laboratory instruction consisting of six hours of laboratory time per week. The first half is devoted to a study of the chemistry of some important nonmetals and the demonstration of chemical principles which are essential for the understanding of chemical theories and laws. The second half deals with qualitiative analysis of both cations and anions in a routine manner. Although this manual was prepared primarily to accompany the authors' 'First Year College Chemistry' text, it should prove satisfactory for use with other texts. The sequence in which the experiments are performed could be changed to conform with the material in another text." (Quoted from authors' preface.)

In general the experiments are of conventional types. Several are quantitative. "The scheme of qualitative analysis is a more or less conventional hydrogen sulfide system. One variation is the use of sodium sulfide rather than the polysulfide in the separation of the copper and arsenic groups," following oxidation of stannous to stannic. (Quotation from preface.) Parallel procedures, semimicro and macro, are given for the analyses, including specific, step-by-step instructions. The approach followed can perhaps best be characterized by quoting from the preliminary instructions on page 134: "For each group a schematic method of separation and identification is given. . . . Study the analytical scheme carefully, and transpose it to the flow-sheet form. . . . To expedite your work, this flow chart should be learned in its entirety. . . . Obtain a sample. . .which contains all the cations of the group to be analyzed. Follow the schematic method of analysis, checking at each point with the flow chart. . . ."

The manual provides blank spaces in which answers are to be written. The pages are perforated and punched, so that they can be torn out as used, and kept in a three-ring binder, or the paper-covered manual can be kept intact. The drawings and directions are clear, and the general make-up of the book is attractive.

WILLIAM E. MORRELL

University of Illinois
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## ● ESSENTIALS OF EXPERIMENTAL CHEMISTRY

*Alfred Benjamin Garrett, Joseph Frederic Haskins, Harry Hall Sisler,* and *Margaret H. Kurbatov,* all of the Ohio State University. Ginn and Co., Boston, 1951. x + 326 pp. 102 figs. 19.5 × 26.5 cm. $2.80.

This is a laboratory manual containing 73 experiments designed for use either as student experiments, as lecture demonstrations, or as a combination of both. Sufficient choice and variety is included to allow for selection or alternation of experiments. Nine experiments require no laboratory work. Only a few experiments involve quantitative technique. Experiments are grouped in eight units of related interests. No qualitative analysis is included.

This manual is written for terminal students of average ability with no previous experience in chemistry. Explanations and directions are detailed with many questions regarding all phases of the work. The emphasis on descriptive material makes this book more suitable for students with nonmathematical interests such as agriculture and home economics.

Pages are perforated to hand in and are punched to fit a standard note book. Also included in the appendix are lists of apparatus needed and quantities of reagents for ten students.

## ● LABORATORY MANUAL FOR BRIEF COLLEGE CHEMISTRY

*Leon B. Richardson,* Emeritus Professor of Chemistry, Dartmouth College, and *Andrew J. Scarlett,* Professor of Chemistry, Dartmouth College. Revised edition. Henry Holt and Co., New York, 1951. viii + 232 pp. 18 figs. 21.5 × 28 cm. Spring binding. $2.

The 51 experiments in this manual are of varying length and are designed for an elementary class of average students. Although a few of the experiments are quantitative the emphasis is on descriptive material. No preliminary discussion is included in experiments and directions concerning technique are kept to a minimum. Report sheets with questions and spaces for answers are included. There is no systematic qualitative analysis except for anions, the tests for cations being parts of experiments on the individual metals. Only four organic experiments are included.

## ● LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS

*George W. Watt,* Professor of Chemistry, University of Texas. Second edition. McGraw-Hill Book Co., Inc., New York, 1951. x + 230 pp. 47 figs. 24 × 28 cm. Spring binding. $2.75.

The first part of this book consists of 49 general and inorganic experiments. Directions are complete, questions are thought-provoking, but only a minimum of introductory discussion is given. Many experiments were adapted from directions given in papers published in This Journal and references are included. A very large proportion of the experiments are quantitative in approach. A desirable feature is the insistence on safety precautions, including approval of apparatus.

The latter portion of the book is devoted to a standard systematic scheme of qualitative analysis, using $H_2S$. Directions are clear and flow sheets are given. Report pages for both knowns and unknowns are included.

Pages are perforated for reports to be handed in and are punched to fit a standard note book. Lists of apparatus and of reagents needed for experiments are in the appendix.

## ● EXPERIMENTAL STUDIES IN BASIC COLLEGE CHEMISTRY

*Everette L. Henderson,* Professor of Chemistry, University of Detroit. Thomas Y. Crowell Co., New York, 1951. x + 246 pp. 48 figs. 3 graphs. 20 × 27 cm. $2.50.

There are 48 experiments of approximately equal length in this manual. Directions are complete and easily understood, preceded by discussion of principles involved and followed by review questions and problems. Spaces are included for results and answers to questions. The arrangement of the book is such that pages must be left attached and the whole book handed in for correction. No qualitative analysis and only three organic experiments are included.

## ● CHEMICAL SYMBOLISM AND CALCULATIONS

*Stanley W. Morse,* Professor of Physical Science, San Francisco State College. The National Press, Millbrae, Calif., 1950. viii + 144 pp. 4 tables. 22 × 27.5 cm. Spiral binding $2.

This workbook is intended for use as a supplement to any regular textbook in general chemistry. It supplies more detailed directions about use of symbols, formulas, equations, and the solving of problems of all kinds than most textbooks do. In each section of the book there is a review of the principles involved, examples of each kind are solved with accompanying explanation, sets of practice problems are given with answers, and

finally assignment sheets of problems without answers are included. Sufficient problems are listed so that each teacher can select or reject at will.

Methods used to illustrate the solution of problems are based on an understanding of principles rather than on memorization of formulas. Careful analysis of the problem before undertaking its solution is emphasized. Teachers favoring this approach should find this book very useful.

## ● A LABORATORY MANUAL OF GENERAL CHEMISTRY

*John H. Secrist, Karl H. Gayer,* and *Richard B. Hahn,* Assistant Professors of Chemistry, Wayne University. Wm. C. Brown Co., Dubuque, Iowa, 1951. viii + 199 pp. 35 figs. 22 × 28 cm. Spiral binding $2.75.

IN THIS manual there are 46 experiments. The emphasis is more on fundamental principles and quantitative relationships than is usual in most first year courses. Another departure from the average course is the authors' use of the laboratory quiz to supplant the usual laboratory notes or answers to questions. In this manual the only papers to be handed in are the data sheets, which, in most cases, contain only the quantitative data and calculations. A list of study questions is given at the end of each experiment and a quiz on some of these questions is to be given at the end of each days work.

Lists of reagents required for the experiments are appended.

## ● GENERAL CHEMISTRY FOR LABORATORIES

*Jelks Barksdale,* Alabama Polytechnic Institute. Longmans, Green and Co., New York, 1951. xiii + 152 pp. 24 figs. 21.5 × 28 cm. $1.50.

THERE are 87 experiments in this manual varying in length from a single operation to those requiring several hours. Previous knowledge of chemistry is not required but the successful completion of the exercises requires the student to carefully observe and interpret results. Directions are brief and explanations are kept to a minimum. Questions are thought provoking.

The manual is essentially inorganic, the only organic experiments include 1 being those referring to hydrocarbons and fuels. Many tests for metallic and nonmetallic ions are given but no systematic scheme of qualitative analysis is included.

Space is allowed for answers to questions but no provision is made for removing pages to hand in experiments.

## ● CHEMISTRY FOR THE LABORATORY

*Alfred B. Garrett, Joseph F. Haskins, Thor R. Rubin,* and *Frank H. Verhoek,* all of the Ohio State University. Ginn and Co., Boston, 1951. xi + 355 pp. 145 figs. 19.5 × 26.5 cm. $3.

THIS manual contains 78 experiments written for beginning students of average ability. Many experiments, especially in the first half of the book, are quantitative. Throughout the emphasis is on the needs of students in engineering and other nonchemical fields. Directions, explanations, and questions are complete and usually simple and easily understandable. Many of the individual tests and general principles of qualitative analysis are used, but no systematic scheme of analysis is included. There are 12 experiments on organic materials. Experiments vary considerably in length.

Pages are perforated to hand in and punched to fit a standard note book. Spaces are allowed for writing in answers to questions. Complete lists of apparatus and quantities of reagents needed for ten students are included in the appendix.

FRED C. FREYTAG

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## ● MANIPULATIONS DE CHIMIE

*Clément Duval,* University of Paris. Second edition. Masson & Cie., Paris, 1951. 382 pp. 65 figs. 21 tables. 15 × 24 cm. 2500 francs.

THIS collection of more than 700 procedures for preparing inorganic and organic substances is intended to teach the various types of manipulations. The starting materials are inexpensive; the time for any one preparation is not more than a week; the apparatus can be readily assembled or constructed from standard parts.

The operations are planned to illustrate general laws and rules, hence the exercises reinforce what has been stated in the lectures. Physical constants are given to enable the student to identify his product or to check its purity. Analytical operations have been omitted except with respect to the preparation of derivatives characterizing organic functional groups. Although most of the important types of reactions have been included, certain ones have been passed over because they involve no new and significant technique or because they are not suited to large classes.

For the most part the procedures are taken directly from the literature (the literature references are given) though frequently the directions are modified because the author has found that the yields can be improved by changes or by paying particular care to certain details. The preparations are grouped by methods rather than by chemical relationships, since two materials of the same kind sometimes require very distinct types of preparational procedures; *e. g.*, selenious oxide (solid) and sulfurous oxide (gas).

The inorganic portion covers 138 pages, the organic part, 187. The indexes are unusually complete. The placing of the necessary tables in the beginning of the text comes as a surprise to the American reader.

The book has certain defects, though these are not too serious if it is remembered that this is a teaching tool and not a reference volume. Most of the procedures are rather old and better methods are now available. The directions are none too full in certain cases and the literature will have to be consulted by the independent worker, an obvious drawback in some localities. Hazards are not stressed, such as danger of fires or explosions, toxicity of products, etc. A few mistakes in formulas were noted; morpholine (page 305); diazomethane (page 306) for instance. The introductory remarks (*Generalities*) of the various divisions are rather sketchy and of small actual value.

The book is well printed; the figures are clear and well drawn.

The text has obviously found favor in French schools but its place in the usual American curriculum is problematical. Nevertheless, it would be a good addition to the departmental library, where it could be used as a source of possible procedures and especially as a fine collection of exercises for those wishing to gain facility in reading chemical French.

RALPH E. OESPER

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## ● VINYL AND RELATED PLASTICS

*Calvin E. Schildknecht,* Celanese Corporation of America, Summit, New Jersey. John Wiley & Sons, Inc., New York, 1952. xi + 723 pp. Illustrated. 15 × 23.5 cm. $12.50.

SELDOM is such a wealth of information presented in such readable style as is achieved in this book.

The subject has become one of foremost industrial importance in the last fifteen years, and the author has given major emphasis to its practical aspects. However it is difficult to get access to information that is regarded as the competitive stock-in-trade of industrial concerns. In many cases, however, the patent literature has been supplemented with descriptions of related products and processes which were developed in Germany and

described since the war in detailed reports by technical teams. With his own experience in evaluating the commercial practicability of published examples and claims, the author has presented a survey that is comprehensive indeed. The literature appears to have been covered with painstaking care and judicious appraisal. The book contains over 4000 references dating from 1835 to the second half of 1951.

Topics covered are: styrene polymerization (written as an introduction to polymer science); styrene copolymerization; styrene derivative and related polymers; methacrylic and acrylic ester polymers; acrylonitrile, acrylic acid, and related polymers; polymers from vinyl acetate and related monomers; vinyl chloride polymers; vinylidene chloride and fluorovinyl polymers; ethylene high polymers and copolymers; high polymers and copolymers of isobutylene; vinyl ether polymers; sulfur-vinyl compounds; nitrogen-vinyl polymers; vinyl ketone and miscellaneous polymers.

The book is stoutly bound, printed on paper of good quality, and contains remarkably few typographical errors for a first edition. Its price notwithstanding, this book should appeal to nearly every chemist, whether its value be directly related to his own activities in the polymer field or a matter of his being informed on a timely and important subject. It will certainly be recommended by the industrial research staff to the recent graduate who is starting a career concerned with vinyl polymers. There is every reason to hope and expect that this book will find its way into the classroom.

ELLINGTON M. BEAVERS

ROHM AND HAAS CO.
PHILADELPHIA, PENNSYLVANIA

## ● THE SURFACE CHEMISTRY OF SOLIDS

***S. J. Gregg,* Reader in Surface Chemistry, University College of the South West of England, Exeter. Reinhold Publishing Corp., New York, 1951. ix + 297 pp. 105 figs. 8 tables. 14.5 × 22.5 cm. $8.50.**

THIS little book is a survey of a widely dispersed field of investigation—the phenomena which occur at the surface of a solid. The author's attempt has been to systematize the information, both empirical and theoretical, in terms of principles and thus to indicate the present status of knowledge of the subject. The result is that he has produced a valuable book which occupies a position in the scientific literature midway between an exhaustive treatise, useful as a reference work, and an uncritical, qualitative presentation suitable only as an introduction to the subject. The topics treated range from the contrasting theories of multilayer physical adsorption of gases on solids to the soldering of metals; from catalysis and chemisorption to the water repellancy of ducks' feathers.

A unique feature of this book is the author's apparent reluctance to be drawn into discussions of those surface phenomena which are traditionally classified as "colloid" chemistry. He defends the arbitrariness of this by suggesting that these are "such important subjects in their own right that it would be somewhat forced to regard them as subdivisions of surface chemistry." This point of view results in the complete omission of all mention of the manifold effects of the adsorption of ions by colloidally dispersed solids, etc. The choice of subject matter emphasizes, rather, the significance of surface effects (particularly adsorption) in the ordinary chemical and physical interactions of matter. For example, there are chapters devoted to Adhesion and the Effect of Adsorption on It, The Spreading of a Liquid over a Solid, and The Part Played by Surface in Chemical Reactions. Experimental techniques pertinent to the problems of surface chemistry are described. These range from the accurate determination of densities in various liquids to the electron microscopy of surfaces. A great variety of applications to the practical problems of industry (such as friction and lubrication) are indicated.

The phenomena associated with the adsorption of gases by solids receive considerable detailed review. These discussions rather unfortunately are broken into isolated portions by the chapter arrangements. Clear-cut distinction between physical adsorption and chemisorption is not immediately apparent. Incorrect impressions might result from casual inspection or piecemeal reading of these sections.

Students in introductory physical chemistry courses will find this book interesting and valuable as supplementary reading. It certainly belongs on encyclopedic library shelves. It is very readable and amply illustrated. The photographs and electron micrographs are well chosen and clearly reproduced. The author provides each chapter with a concise summary, a list of references and a short bibliography.

WILLIAM F. KIEFFER

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## ● THE NATURE OF SOME OF OUR PHYSICAL CONCEPTS

***P. W. Bridgman,* Professor of Physics, Harvard. Philosophical Library, New York, 1952. 64 pp. 4 figs. 15.5 × 23.5 cm. $2.75.**

THIS book presents three lectures which were given in 1950 under the auspices of the Department of the History and Philosophy of Science at City College, University of London. They were published in the January, April, and August, 1951, numbers of the *British Journal for the Philosophy of Science.* In subject matter, they represent an even more penetrating analysis of certain physical concepts than the author has given in his books, "The Logic of Modern Physics," "The Nature of Thermodynamics," and "The Thermodynamics of Electrical Phenomena in Metals."

The first lecture takes up the general operational approach, and shows how in our concepts we jump back and forth between instrumental operations and mental operations. The mathematician may say, "We will now perform the operation of differentiating this equation," but his "operation" does not mean the same as that of the physicist who says, "I will now take my ruler and measure this object."

The second lecture is concerned with thermodynamics. Operational definitions necessarily refer to those concepts that are not dependent upon any postulated structural thory of matter. Thus they can be applied to thermodynamics, because *if* (imagining the impossible) the atomic theory were disproved tomorrow thermodynamics would remain. By the operational definition of entropy we can only speak of the entropy of a body if there exists some reversible way of reaching its state. "But many of the bodies of experience are in such a state that every change to which the body is subjected contains some component of irreversibility. An example is any piece of metal which has been heavily strained plastically.... Incidentally, the whole living world of biology is thus isolated.... For if the entropy concept were applicable, it would involve some reversible method of getting from the nonliving to the living, and this involves at the least the artificial creation of life, an operation which we cannot at present perform." Undeterred by this difficulty, Professor Bridgman suggests the lines of a possible extension of the concept of entropy whereby "we may attack the problem by methods in the spirit, if not the letter, of classical thermodynamics."

Classical physics makes frequent use of "mental experiments." A unit charge is introduced into a "field," and the force of it is measured; a smaller charge is then introduced, and then successively smaller ones, and the limit of force per unit charge is taken. Another example is the familiar "Carnot's engine" with its highly unreal system of perfect conductors and perfect insulators, which can be approached by a theoretical infinitely slow operation taking infinite time. By such devices "usually it is possible to give the system such dimensions or otherwise modify it so that the irreversible aspects may be made vanishingly small in comparison with the reversible ones." But in a thermo-

electric circuit there are *two* irreversible processes, thermal conduction and Joulean heating, so interconnected that any device that approaches one to reversibility necessarily drives the other far into irreversibility. Kelvin tackled this problem by means of what he realized was an "illegal operation." Bridgman seriously considers this problem in the third lecture. He utilizes experimental results on single metal crystals which were not available to Kelvin, and with the aid of these and of several new concepts from the domain of paper-and-pencil operations, restores legitimacy to the situation.

In spite of the agreement between the verbal and instrumental components of science which Professor Bridgman works so hard to achieve, the mental content of this slim volume is quite out of proportion to its physical size.

ANTHONY STANDEN

THE INTERSCIENCE ENCYCLOPEDIA
BROOKLYN, NEW YORK

## • A. F. HOLLEMAN'S ORGANIC CHEMISTRY

***J. P. Wibaut,* Professor of Organic Chemistry, University of Amsterdam. Translated from the sixteenth Dutch edition by *S. Coffey,* I.C.I. Dyestuffs Division, Manchester. Elsevier Publishing Co., Inc., Houston, Texas, 1951. xvi + 622 pp. 66 figs. 51 tables. 18 × 26 cm. $9.**

HOLLEMAN'S original "Organic Chemistry" has been through fifteen previous Dutch editions and was last translated into English in 1930. The present edition was undertaken by Prof. Wibaut "with special care being taken that the original character of the book should be retained," *i. e.,* the subject matter should be treated from both a structural and physicochemical viewpoint. The book is intended for students of chemistry, biology, and medicine, and is divided into sections on general aspects, aliphatic, polyfunctional aliphatic, aromatic, alicyclic, and heterocyclic compounds. The text attempts to provide a broad elementary background in the science as well as a survey of more recent developments of theoretical or practical importance. Toward a fulfillment of the latter objective fine print paragraphs are frequently inserted into the main textual material, and throughout the book specific material of more recent origin and advanced nature is to be found in such sections. Wherever appropriate there is included a brief discussion of the classical chemical evidence upon which accepted structural formulas are based, including data from both degradative and synthetic sources. Names of original investigators are widely given and the book includes a six-page author index. Unfortunately, the dates of investigations are not generally included, however, and the text is of little value as a guide to the original literature.

Criticisms of the text fall into both general and specific categories. Generally speaking, it appears to this reviewer that the book attempts perhaps too much for one of its size. The dividing line between elementary and advanced material seems rather more abrupt than desirable for the beginning student. Thus, for example, the more advanced matter in the fine-print sections mentioned previously is not always obviously related to the more elementary material preceding it, suggesting the possibility of confusion for the unsophisticated reader. More serious, perhaps, is the author's rather fragmented approach to the subject. The underlying general relationships among organic reactions are by no means clearly delineated from the viewpoints of mechanism or analogy, and the reader is left with little appreciation of more recent unifying trends in the science. The nonunified approach has the further result of considerable unnecessary repetition in some sections, and the freshness and spontaneity of the translation suffer occasionally thereby. The author's treatment of his material seems in general a little noncritical; yields, side reactions, and in particular limitations of organic reactions, seldom receive consideration. Discussions frequently contain undefined or poorly defined terms, introducing a further source of confusion to the beginner.

More specific criticsims vary in importance and are indeed too numerous to tabulate in detail. Suggestions in the preface to the contrary notwithstanding, there is very little adequate treatment of theoretical material in the text. Where such is included, it is not correlated with other material in places where correlation might be possible. Certain physicochemical subjects such as thermochemistry and molecular refraction receive treatment the detail of which seems out of proportion for a general text, while others such as spectrographic and kinetic techniques receive too superficial a treatment. Many important topics receive what this reviewer feels to be somewhat inadequate consideration on either the descriptive or theoretical sides. Among such topics are spectra and constitution, organometallic compounds, free radicals, molecular rearrangements, structure and reactivity, optical and geometrical isomerism, polymerization, certain natural products, and industrial or technological considerations. To be sure, discussion of such subjects is not totally absent, but treatment seems inadequate as a result of either excessive brevity, dilution with extraneous material, or lack of correlation among widely distributed examples. Organic nomenclature receives a distinctly superficial treatment, no attempt being made to develop a systematic approach to the subject. This fact, combined with an absence of illustrative problems, further insures the text's inadequacy for a beginning student. Such mechanistic material as has been included is frequently outdated and presented noncritically with only limited emphasis on supporting experimental data. The concepts behind and applications of resonance theory are handled with an undesirable brevity.

While the number of factual errors in the book appears low, errors in nomenclature and typography are not infrequent. The book was obviously read carelessly in proof. Punctuation, typography, and style lack in uniformity throughout the book. In many places economy as well as generality would have been achieved by a greater reliance on equations or tables in place of verbal description. Equations given are stylistically nonuniform, frequently not balanced, and lacking in the expression of specific conditions over the arrow. Occasional analogies are drawn from inorganic chemistry that are erroneous in the light of current theory. Perhaps because of the fragmented approach to the material, the subject index is far from adequate. There are, for example, only two entries each under mesomerism and oxidation, one entry each under alkylation and nitration, and no entries under halogenation, reduction, sulfonation, acidity, or molecular rearrangements. Printed on heavy paper and weighing over four pounds the book is cumbersome and uncomfortable to read.

Attempting at once to be both elementary and advanced, it is perhaps surprising that a book of this size can be as adequate as the present is. The inadequacies resulting almost inevitably in an attempt of the present sort, however, make it difficult to recommend the book either for the beginning or more advanced student of organic chemistry.

WILLIAM A. BONNER

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## • HANDBOOK OF DANGEROUS MATERIALS

***N. Irving Sax,* Toxicologist, General Electric Co. Assisted by *M. J. O'Herin,* Fungicide Laboratory, General Electric Co., and *W. W. Schultz,* General Engineering Laboratory, General Electric Co. Reinhold Publishing Corp., New York, 1951. vii + 848 pp. Illustrated. 18.5 × 26 cm. $15.**

THIS book is divided into the following sections: (1) General Chemicals: Under this heading there is a listing of 5000 dangerous materials, together with information regarding hazardous properties, treatment, antidotes, extinguishers, storage and handling, personnel safety precautions, physical properties (flash point, autoignition point, etc.), shipping regulations and labeling instructions. (2) Explosives: Surface storage of explosives, destruction of explosives, chemical ammunition and miscellaneous explosives, high explosives and low explosives.

(3) Fungus Diseases and Fungicides. (4) Radiation and Radiation Hazards. (5) Shipping Regulations. In addition the book contains references which the authors have utilized, and also a list of abbreviations and symbols and a general index.

According to the authors, "this book is directed to not only the industrial physician and trained safety inspector in industry, but to foremen and plant managers, who have neither the time or the inclination to make a deep study of possible toxic hazards that might occur in their shops. It is also intended for research and development laboratories and pilot plant workers who use a wide variety of materials and who often need reliable safety data concerning them."

This reviewer believes that this is undoubtedly one of the most extensive reference books of its kind. The material is arranged alphabetically, contains a cross reference and, as stated, an index. Concerning the general chemicals, a synonym is given for each one as well as its formula, flash point, density, and melting and boiling points. Whenever necessary shipping regulations are also stated, and in addition the hazardous properties of many of the chemicals are described.

Occasionally, statements made regarding toxic properties of many of the chemicals mentioned are not sufficiently specific and often create an erroneous impression of the existing hazard. For instance, under a description of the hazardous properties of aniline it is stated that, "this hazard was first discovered in the German dye industry where the 'aniline tumor' was said to develop in men exposed to it. In modern times and with present methods of handling, the occurrence of any serious poisoning in industry has been prevented." This statement would indicate that it was the method of handling aniline which has now prevented the aniline tumor. Actually, it is now known that it is not aniline which caused the bladder tumors but rather the $\beta$-naphthylamine and benzidine utilized in the dye industry that are carcinogenic. Other instances in which there is not sufficient attention given to the concentration, the length of exposure, and specific effects to certain organs of the body could be cited. As a whole, the chemicals are dealt with in a very excellent manner, but this book should not be considered as a textbook on industrial toxicology.

This reviewer has not seen in any other book such complete coverage of the explosives and shipping regulations as is found here. This reviewer is not qualified to comment on the chapter on radiation although it appears to be most complete, and scientific.

Section three deals with the fungus diseases and the fungicides. It gives a table of fungus disease in industry which includes agriculture workers, bakers, dairymen, chambermaids, grape pickers, jockeys, squab feeders, bath house attendants, and numerous other occupations. In addition the section takes up the toxicity of fungicides and considers a wide variety of these in alphabetical order.

RUTHERFORD T. JOHNSTONE

Los Angeles
California

## ● WORLD POPULATION AND FUTURE RESOURCES

**Edited by *Paul K. Hatt*, Professor of Sociology, Northwestern University. The Proceedings of the Second Centennial Academic Conference of Northwestern University. American Book Co., New York, 1951. xviii + 262 pp. Illustrated. 14.5 × 21.5 cm. $3.50.**

In this symposium of views by 20 participants on population, food resources, and the mineral and energy supplies for the future, the general prospect is, on the whole, not too optimistic. The population problem is complicated by our political and economic barriers and is not amenable to rational treatment as long as these barriers prevail. In this connection we find that the term "ecosystem" has invaded sociological literature, and that the grim possibility of mass reduction of populations by widespread mortalities, such as the Black Death, is seriously considered. While the chapters on mineral and energy resources do not provide too much precise data, they do constitute a useful general summary which, is on the whole, a level-headed and conservative appraisal of such resources. Unfortunately, however, one of the most critical resource problems, that of fertilizers, is mentioned only in the discussion of land development; it deserves more detailed treatment; for here we may have the weakest link in our chain. The implicit moral of the whole symposium is that we must think, not in terms of raising the underprivileged to our standards, but in sacrificing some of our own to meet on some middle ground, if mankind is to survive in anything like the numbers which now inhabit the earth.

J. W. HEDGPETH

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## ● THE AMINO ACID COMPOSITION OF PROTEINS AND FOODS

**_Richard J. Block_, Department of Physiology and Biochemistry, New York Medical College, and _Diane Bolling_. Second edition. Charles C Thomas, Springfield, Ill., 1951. xxxviii + 576 pp. Illustrated. 16 × 25 cm. $10.50.**

The appearance of a second edition of this book, five years after the first edition, testifies to its favorable reception by protein chemists. This is a volume definitely for the use of the analytical chemist who is concerned with the analysis of proteins for their amino-acid content. The knowledge, gained a few decades ago, that the nutritive value of protein depends upon the protein's content of certain amino acids has emphasized the necessity of accurate evaluation of the amino-acid make-up of pure proteins and protein foods. Such analysis presents a difficult problem and involves many pitfalls. Much work has been done and many methods have been developed.

The authors of this volume have critically evaluated analytical methods for amino-acid determinations from the classical methods based on isolation of individual amino acids to the newer procedures involving chromatography, isotope dilution and microbiological techniques. The destruction of amino acids during hydrolysis of the proteins prior to analysis and methods for minimizing such destruction are considered in detail. This loss represents one of the chief errors in protein analysis and is frequently neglected in evaluating results of amino-acid analysis.

In the early chapters of the book the analytical methods for individual amino acids are presented. These are grouped under the following headings: diamino acids, aromatic amino acids, sulfur containing amino acids, $\beta$-hydroxy amino acids, the "leucine" amino acids, dicarboxylic amino acids, glycine and alanine, proline and hydroxyproline. In each of the chapters, following the description of the analytical methods, the composition of proteins and protein foods with respect to the amino acids under discussion are given in tables. The data, taken from the literature, have been calculated to 16.0 grams of nitrogen. That is, the grams of amino acids given in tables represent the amount that would be obtained from that quantity of protein containing 16 grams of nitrogen. The amino-acid composition of proteins is also summarized in extensive tables near the end of the book. A hundred pages are devoted to a discussion of general methods for protein analysis. In this part are included preparation of the sample for analysis, methods and conditions of hydrolysis, separation of amino acids by fractional distillation of their esters, electrolytic separation, chromotography, including paper chromatography. Microbiological and enzymatic methods of analysis are described.

Using the data on amino-acid make-up of food proteins and the well-known food consumption surveys conducted some years ago by the Department of Agriculture, the authors calculate the amino-acid intake on typical American dietaries. The amino-acid contribution of specific food groups, as consumed, is also evaluated.

From the brief description given in this review, it should be

evident that most of the problems that the amino-acid analyst will encounter have been considered by the authors. The value of the book is further enhanced by the extensive data which it contains of the amino-acid composition of aninal and plant proteins, individually and as they occur in foods.

F. A. CAJORI

University of Colorado School of Medicine
Denver, Colorado

## ● COLOR IN BUSINESS, SCIENCE, AND INDUSTRY

***Deane B. Judd,*** **Chief of the Colorimetry Unit, National Bureau of Standards, Washington, D. C. John Wiley & Sons, Inc., New York, 1952. ix + 401 pp. 106 figs. 25 tables. 15 × 23 cm. $6.50.**

Metallurgists are concerned primarily with a physical property, such as hardness, in a steel, and only secondarily with the nature of the components and/or their amounts. Similarly, chemists and others often are more interested in the color of a product than in what the colorant is or its amount.

The color one perceives in a given case may depend upon various factors, such as the illuminant, the immediate surroundings of the object, the nature and conditions of the object, the conditions of illumination, and the normality of the observer. Thus, color is not a simple property of objects, as is mass or volume. Consequently, discussion of the different aspects of color is a difficult assignment. It is not easy, either, to measure or specify color.

To deal with this problem, Dr. Judd brings rare ability to write clearly and accurately. Associated with the National Bureau of Standards for a quarter of a century, he has dealt with a large number of diversified color problems. His own contributions to colorimetry have brought him international renown. Drawing upon this wealth of personal experience and knowledge he has produced an outstanding book on color.

Part I (79 pages) summarizes basic facts of the process of color vision. Included are discussions of physical, chemical, physiological, physchological, and psychophysical factors.

Part II (216 pages) deals with tools and techniques. This long section covers broadly the instrumental and related means used for measuring, specifying, or describing color. The material ranges from the international C.I.E. spectrophotometric determination of $x$, $y$ chromaticity coordinates to word designation by means of the system recommended by the Intersociety Color Council-National Bureau of Standards.

Part III (53 pages) relates to the physics and psychophysics of colorant layers. Included are the general theory of gloss and opacity or hiding power, together with suggestions on the problems of identifying and/or formulating colorants.

The Appendix contains tabular data useful for calculations. A general bibliography on color and a good subject index follow.

The book as a whole is another example of Dr. Judd's excellent work. The reviewer recommends it.

M. G. MELLON

Purdue University
Lafayette, Indiana

## ● DOSAGES COLORIMÉTRIQUES

***G. Charlot,*** **Professeur à l'École Supérieure de Physique et de Chimie Industrielles, and** ***R. Gauguin,*** **Sous-chef de travaux à l'École Supérieure de Physique et de Chimie Industrielles. Masson et Cie., Paris, 1952. 243 pp. 42 figs. 16 × 25 cm. 1500 francs.**

This new book is divided into two main sections: (1) general principles of absorptimetric measurements in the visual region of the spectrum; and (2) a résumé of the better known methods applicable to the determination of 58 elements, exclusive of the rare earth group. A dozen nonmetals are included.

Part one, (94 pages), is subdivided into the following six chapters: I. Beer's Law, with Consideration of It's Validity; II. General Principles of Visual and Photoelectric Methods of Measurement; III. Precision in Visual and Photoelectric Determinations; IV. Details of Making Colorimetric Determinations; V. Separation of Traces by Precipitation, Liquid-Liquid Extraction, Selective Adsorption, Distillation, and Electrodeposition; and VI. Methods Based on Fluorimetry, Turbidimetry, and Nephelometry.

Part two, (144 pages), summarizes concisely the facts on which the procedures for each method are based. Application to specific material is not included.

Iron may be taken as an example. Separations include precipitation as sulfide, hydrous oxide, cupferrate, or oxinate, and extraction as chloroferrate, cupferrate, or oxinate. Pure iron and Mohr's salt are suggested standards. Various details are given for the two selected color-forming reagents, thiocyanate and 1,10-phenanthroline, with many references to recent literature on them. In addition, references are given for a half-dozen other reagents.

Although the detail of coverage is not comparable to that in the book by Sandell, or in the set by Snell and Snell, the reviewer likes the work as a whole. The arrangement is good, the methods seem well selected, and the references are adequate. The French style appeals to him.

The addition of subject and author indexes and the use of better binding would be improvements.

M. G. MELLON

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Lafayette, Indiana

## ● INDUSTRIAL OIL AND FAT PRODUCTS

***Alton E. Bailey,*** **Director of Research, The Humko Company, Memphis, Tenn. Second edition. Interscience Publishers, Inc., New York, 1951. xxiv + 967 pp. 164 figs. 131 tables. 15 × 23.5 cm. $15.**

As a general reference work on modern technology in the oil and fat industries, this text stands quite alone. It is a book that was crying to be written for years before the appearance of its first edition in 1945, and no need was ever more satisfactorily supplied.

"Industrial Oil and Fat Products" covers more than its title implies. Its opening sections on (*a*) The Nature of Fats and Oils and (*b*) Raw Materials for Oil and Fat Products, occupying nearly 200 pages, can be recommended to the advanced student as probably the most satisfactory summary he will find anywhere of the present state of our knowledge of the chemistry of fats and oils. And in the two remaining sections, (*c*) Industrial Utilization of Fats and Oils and (*d*) Unit Processes in Oil and Fat Technology, the descriptions of current industrial practices and their historical development are supplemented by extended discussions of underlying chemical and physicochemical theory.

The author writes most authoritatively and most interestingly in his own field of specialization, the processing and utilization of edible fats, but he is equally thorough in the rest of the book where he had necessarily to rely more fully upon published information and the assistance of colleagues. The industrial products to which separate chapters are devoted include: cooking and salad oils and salad dressings; plastic shortening agents; butter and margarine; bakery products and confections; soap and other surface-active agents; paints, varnishes, and related products; and miscellaneous products from drying and nondrying oils. The unit processes dealt with are: handling, storage and grading of oils and oil-bearing materials; extraction of fats and oils; refining and bleaching; hydrogenation; deodorization; fat splitting, esterification and interesterification; soapmaking; fractionation of fats and fatty acids; polymerization, isomerization, and related processes; solidification, homogenization, and emulsification.

In this second edition the text has been extensively revised and much of it entirely rewritten to incorporate the advances in re-

search and technology of the intervening years. It is larger by a third, despite the elimination of an entire chapter on Production and Consumption occasioned in part by the inadequacy of recent world-wide statistical data. A greatly expanded and correspondingly more useful table of contents is now provided, and further improvement has been effected in a number of places by rearrangement of subject matter into more logical order within the chapters. The hundreds of literature references are carried as footnotes to the text and numbered serially within each chapter. Both author and subject indexes are provided.

The book is of pleasing design and sturdy construction, conforming in all its physical features to the high standard set by the publishers for the series of monographs on Fats and Oils of which this volume is one.

ROBERT N. WENZEL

Westinghouse Research Laboratories
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## ● PRINCIPLES OF QUANTUM MECHANICS

***William V. Houston,*** **The Rice Institute. McGraw-Hill Book Co., Inc., New York, 1951. vii + 288 pp. Illustrated. 16 × 23.5 cm. $6.**

For this beginning book in quantum mechanics, the author presupposes a knowledge of elementary mathematical physics, including such things as vector analysis and electromagnetic theory. After a brief historical introduction he proceeds, in the third chapter, to develop Schrödinger's equations, including the effect of an electromagnetic field. The problems that can be solved exactly are then taken up. Perturbation theory and the variation method are followed by spin theory, one electron spectra, and two electron spectra. Collision problems then precede the electron theory of solids. The book ends with applications to electromagnetic theory.

The book is well written and will be enjoyed by those who have the preparation which a good graduate student in physics should have. Chemists will not find even the hydrogen molecule treated, but will find the book a valuable treatment of the fundamentals with many interesting physical examples.

HENRY EYRING

University of Utah
Salt Lake City, Utah

## ● PHYSICAL PROPERTIES AND ANALYSIS OF HEAVY WATER

***Isidor Kirshenbaum,*** **Esso Laboratories, Standard Oil Development Company. Edited by *Harold C. Urey,* Institute for Nuclear Studies, University of Chicago, and *George M. Murphy,* Washington Square College, New York University. McGraw-Hill Book Co., Inc., New York, 1951. xv + 438 pp. 150 figs. 15.5 × 23.5 cm. $5.25.**

This volume is one of the National Nuclear Energy Series (Manhattan Project Technical Section). Most of the volume is occupied by description of original research which was performed during the war and which has now been declassified.

The first chapter presents best values of an extensive list of physical properties of heavy water. These are based upon a critical survey of the literature supplemented by further experiments in cases where previous work appeared inconsistent or inaccurate.

The second chapter presents values of equilibrium constants for hydrogen-isotope exchange reactions between hydrogen and water, hydrogen and ammonia, and oxygen-isotope exchange between carbon dioxide and water. The constants are computed by statistical mechanics from spectroscopic data and checked experimentally.

The last chapter deals with the natural abundance of hydrogen and oxygen isotopes. Previous literature is critically surveyed and further experimental work is presented.

The remainder of the book is devoted to methods of isotopic analysis of heavy water. Save for background material, this consists almost entirely of reports of original work. Experimental and computational procedures are presented in considerable detail.

Nearly one half of the book is devoted to isotopic analyses by the mass spectrometer. In view of the current commercial availability of mass spectrometers, the considerable space devoted to constructional details of the mass spectrometers which were employed will probably be of little interest to those primarily interested in isotopic analyses. However, the procedures—preparation of samples, computations, calibrations, etc.—will still be of value.

The remainder of the book is largely devoted to analysis of heavy water for its deuterium content by specific gravity methods: in largest degree to the float method and to the falling drop method. Pycnometric and refractometric procedures are also discussed.

This book will be of considerable interest and assistance to those interested in isotope reactions and will be of particular value to those concerned with istopic analysis. It must have been a rather difficult task to rework the large number of wartime reports upon which the experimental portion of this book rests. The author is to be congratulated upon the success of his effort.

ROBERT L. BURWELL, JR.

Northwestern University
Evanston, Illinois

## ● THE THEORY OF ISOTOPE SEPARATION AS APPLIED TO LARGE-SCALE PRODUCTION OF $U^{235}$

***Karl Cohen,*** **Director, Atomic Energy Division, The H. K. Ferguson Company. Edited by *George M. Murphy,* Washington Square College, New York University. Volume 1B, Division III, National Nuclear Energy Series, Manhattan Project, Technical Section. McGraw-Hill Book Co., Inc., 1951. xviii + 165 pp. Illustrated. 16 × 23.5 cm. $2.**

This volume summarizes the theoretical work of the SAM Laboratories during the period from 1940 to 1945 relating to the centrifugal, electromagnetic, electrolytic, chemical exhange, thermal diffusion, and distillation methods of separating isotopes.

In the first five chapters, the theory of cascades is developed in as general a way as possible to permit extension to other types of separation problems. A discussion of application has been somewhat hampered by existing security restrictions. The book is entirely mathematical and in a terminology that is strange to chemists. The obvious importance of the subject, however, makes it mandatory on departments of chemical engineering to become familiar with the theories of separations, and to extend them to new developments. This book will be of aid in making this extension.

LAURENCE S. FOSTER

Belmont, Massachusetts

## ● THE ALKALOIDS—CHEMISTRY AND PHYSIOLOGY. VOLUME II

**Edited by *R. H. F. Manske,* Dominion Rubber Research Laboratory, Guelph, Ontario, Canada, and *H. L. Holmes,* Riker Laboratories, Inc., Los Angeles. Academic Press, Inc., New York, 1952. viii + 587 pp. 16 × 23.5 cm. $14.50.**

Alkaloids have been an attractive field of research for chemists since the early developmental days of organic chemistry. With new reagents, new synthetic methods, and new instrumental analytical procedures many of the problems which baffled investigators for decades have been successfully concluded in the recent past. The volume of research on alkaloids has so expanded, and current publications in the field have become so numerous, that it is difficult to assemble a book on alkaloids that is not somewhat out of date at the time of issuance. The authors

of Volume II in this series have overcome this difficulty in part by providing two chapters on one subject (morphine), the latter written as short a time as possible before the publication of this book. In another chapter (colchicine) an addendum describes the work subsequent to the writing of the main chapter.

The complex story of morphine and related alkaloids is presented with unusual clarity in two chapters. It is a pity the book appeared too early to include the total synthesis of morphine which was recently published.

The chapter on Strychnos Alkaloids is supplementary to that found in Volume I which covered references to work published up to early 1947. This new material is a condensation of over 30 papers published between that time and 1950. It discusses the newer chemical degradations and the stereochemistry of strychnine.

Each chapter has been well written and the intricate chemistry skilfully organized. The authors, (H. L. Holmes, Gilbert Stork, J. W. Cook, J. D. Loudon, J. R. Price, and Léo Marion), all of whom have had experience in the investigation of alkaloids, have provided most effective résumés for the benefit of the organic chemist.

ROGER ADAMS

University of Illinois
Urbana, Illinois

## • CHEMICAL TRADE NAMES AND COMMERCIAL SYNONYMS

***William Haynes.*** **D. Van Nostrand, Co., Inc., New York, 1951. ix + 279 pp. 15 × 23 cm. $5.50.**

A (Ansbacher): series of paint and varnish pigments.
DDT: dichloro-diphenyl-trichlorethane; insecticide.
Lamaset (Am. Cyanamid): melamine resin; shrinkage control of woolen fabrics.
Quinoline blue: cyanine; dye.
Ayrox (CCC): synthetic resins; compounding and processing rubber.
1-1-1: equal parts of dimethyl phthalate, ethylbexanediol [*sic*], and indalone.
81223 Compound (G.E.): rubber-silicone molding compound.

Mr. Haynes contacted nearly five hundred manufacturers to obtain from them the trade names used for their chemical products. The Patent Gazette and chemical periodicals were checked to bring the trademarks up to January, 1950. A Key to Manufacturers occupies 22 pages; it gives the abbreviation used, the complete name and address of the manufacturer.

The list of trade names and synonyms enumerates over 20,000 special names used in the chemical industry.

This book is valuable to translate the jargon of the chemical industry to exact names or sources of special products.

KENNETH A. KOBE

University of Texas
Austin, Texas

## • AIR POLLUTION

**Proceedings of the United States Technical Conference on Air Pollution. *Louis C. McCabe,* Chairman. McGraw-Hill Book Co., Inc., 1952. xiv + 847 pp. Illustrated. 19 × 26 cm. $12.50.**

This ponderous volume of 847 pages records the proceedings of a Government sponsored interdepartmental conference on atmospheric pollution which convened in Washington, D. C. on May 3–5, 1950. In addition to the specialists of the Government, many outstanding scholars who have made notable contributions to various aspects of the general problem from the research foundations, universities and industry, both in this country and abroad, were invited to participate.

The general program was broken up into seven major segments: agriculture, analytical methods and properties, equipment, health instrumentation, legislation, and meteorology, each dealt with by a separate panel. All seven panels convened simultaneously over the first two days of the conference. The third day was devoted to a plenary session at which reports were made on the programs and findings of the various panels, and discussions were welcomed.

Any detailed sounding of the great pool of information presented by the ninety-seven papers to the panel groups and by the reports and discussions of the general session would go entirely beyond the reasonable limits of space for a book review. There is in this volume a wealth of important and stimulating information on this general topic which in this country has claimed such widespread interest in research laboratories and the public at large.

After a careful reading of the text the reviewer, though suffering somewhat from an acute attack of mental indigestion, felt grateful for the privilege of tapping, within the covers of a single book, such a mine of information so broad in scope and so rich in significant facts. This volume should be a boon both to the veterans and to the newcomers in this confusing field where so many of the basic sciences meet and where, in the past, so many erroneous conceptions have arisen. It brings the reader well up to date, in summary fashion, on all of the chief facets of the subject of air pollution.

The book is surprisingly free from typographical errors for a first edition, and is of the first rank in printing and binding.

ROBERT E. SWAIN

Stanford University
Stanford, California

## • CORROSION GUIDE

***Erich Rabald,*** **Director and Chief Chemist of C. F. Boehringer and Sohne (Germany). Elsevier Press, Inc., Houston, Texas, 1951. vi + 629 pp. 16 figs. 6 tables. 17 × 25 cm. $12.50.**

The purpose of this guide is to show the relative resistance of over 40 important construction materials to corrosion by more than 250 corrosive agents. An introduction of 48 pages gives some elementary material on principles of corrosion, measurement of corrosion resistance, and tells how to use the following 555 pages of tables. A brief table gives the physical properties of the materials considered. The following lengthy table gives the resistance of these materials to corroding agents from acetaldehyde to zinc sulfate. The materials of construction range from aluminum through ferrous and nonferrous alloys, plastics, ceramics, rubber, textiles, to wood.

The physical construction of the tables is unique in that the first left-hand page of the table is folded and opens out beyond the regular page size so that the list of corroding agents is always visible while the table is being used. The typography and binding of the book are excellent.

The degree of resistance of the material to the corroding agent is shown by +, (+), (−), and −. This division into four qualitative groups frequently is too general, for when two materials both are shown as + the user needs some quantitative data to enable him to make an economic balance of corrosion versus cost, or to evaluate all factors. The prospective user then must turn to the chemical literature or trade bulletins, and because the author must have made this search in the preparation of the tables, the references to the original literature would save much time. In addition to giving the degree of resistance, + to −, the types of equipment that are made from the material are given, as pipe, valves, pumps, autoclaves, and the like. Trade names are used infrequently but chemical analyses are given. A table showing the trade names and nominal composition of materials made in the United States would be helpful.

This book will be a good place to start a corrosion survey.

KENNETH A. KOBE

University of Texas
Austin, Texas

## ● MOLYBDENUM COMPOUNDS. THEIR CHEMISTRY AND TECHNOLOGY

*D. H. Killeffer,* Chemical Consultant, and *Arthur Linz,* Vice-President, Climax Molybdenum Co., with a chapter on The Structural Chemistry of Molybdenum by *Linus Pauling,* California Institute of Technology. Interscience Publishers, New York, 1952. xiv + 407 pp. Illustrated. 15 × 23 cm. $10.50.

From the chemical point of view, molybdenum is one of the most complicated of the elements. It shows five oxidation states; it is amphoteric, and it forms a bewildering array of mononuclear and polynuclear complexes. Because it is so interesting, a considerable literature has grown up around it; because it is so difficult, this literature contains many errors and contradictions. The authors of this book, who have had long experience in the processing of molybdenum compounds, have surveyed this literature thoroughly and have summarized what they consider to be the most reliable data. They have done this well and have made a distinct contribution to the literature of inorganic chemistry. Their ability to point out areas which are unexplored or in which more information is needed is particularly valuable.

The chapter on the structural chemistry of molybdenum, by Linus Pauling, gives a brief survey of the structure determinations of many types of molybdenum compounds, and is extremely well done. The chapter on analytical procedures outlines in detail the methods used by the Climax Molybdenum Co.

The latter part of the book is devoted to uses of molybdenum compounds in the laboratory and in industry. The most extensive use is in catalysts, and many patents on such substances have been granted. As Killeffer and Linz point out, much of this patent literature is in error, and the good can be separated from the bad only by detailed investigation. They have not attempted to do this, but give an extensive bibliography.

The uses of molybdenum in the metallic state and in alloys are barely mentioned.

Written by men actively engaged in the molybdenum industry, the book is frankly propagandist. But it is good propaganda, for it is a real scientific contribution. The authors have done well, not only in outlining what is known about the chemistry of molybdenum, but in showing it as an interesting and promising field for research and devolpment.

JOHN C. BAILAR, JR.

University of Illinois
Urbana, Illinois

## ● DIE BIOGENEN AMINE

*M. Guggenheim,* Dr. phil., Dr. med. h.c., Basel. Fourth edition. Interscience Publishers, Inc., New York, 1951. xv + 619 pp. 16.5 × 23.5 cm. $19.50.

The first edition of "Die biogenen Amine" appeared in 1919 and was recognized as an authoritative account of the chemistry of the naturally occurring amines. With the publication of the second edition in 1923 and the third edition in 1940 the author took cognizance of the progress made in this field and provided, in each edition, a comprehensive and scholarly account of the chemistry and biochemistry of this group of physiologically important compounds. This tradition has been continued in the present, fourth, edition of this book, and, as with its predecessors, it almost certainly will be regarded as being indispensable to investigators interested in the chemistry and biochemistry of the nitrogenous bases of natural origin. The literature appears to have been covered through 1949.

A particular feature of the earlier editions was the practice of calling attention to the existence of nitrogenous bases of unknown constitution by providing a separate chapter for these compounds. This practice is continued in the fourth edition but the list has become very much smaller than that of the earlier editions and one gains the impression that future activity in this field of chemistry will emphasize the genesis and function of these compounds rather than their nature. This is also reflected in the greater emphasis, in the fourth edition, which is placed upon enzyme systems in which the naturally occurring amines, or their precursors, may function either as substrates or inhibitors.

Although this book is well printed and has a pleasing format one is shocked at the price one has to pay for these amenities.

CARL NIEMANN

California Institute of Technology
Pasadena, California

## ● COTTRELL: SAMARITAN OF SCIENCE

*Frank Cameron.* Foreward by *Ernest O. Lawrence,* Doubleday & Co., Inc., New York, 1952. 414 pp. 14.5 × 22 cm. $4.50.

The foreword of this fine book about an American described as a man of integrity "whose allegiances were to mankind and to science" was written by Ernest O. Lawrence of the University of California, who wrote: "Frederick Gardner Cottrell was distinguished not only by his own scientific contributions but even more by his generous spirit and his devotion to helping others along the paths of progress."

This book is really a biography but it is also a great story of American industry. The story of the development of helium in Texas while Frederick Cottrell was associated with the U. S. Bureau of Mines and the Fixed Nitrogen Research Laboratory are but two interesting episodes related by Frank Cameron, who read 10,000 letters and documents as well as the diary which Cottrell kept faithfully for 40 years. The whole project required two years of research.

Industry remembers Dr. Cottrell for the Cottrell precipitator, which solved the problem of smoke and dust by precipitating them with electricity of high voltage, in some cases recovering valuable by-products from the precipitated colloidal dust. Until his death in 1948 he was on of the most colorful and leading scientific figures of the century, and yet he remained almost unknown to the layman because of his deliberate self-effacement.

At the age of 23 he went to Germany and worked with the world's gifted physical chemists, Jacob van't Hoff and Wilhelm Ostwald, receiving his degree *summa cum laude.* Three years later when a professor from Berkeley visited Ostwald's laboratory, he asked if any of the men had known Cottrell. The instructor replied: "He is not here now but his spirit is." This is the feeling one gets today while reading "Cottrell: Samaritan of Science."

GRETA OPPE

Ball High School
Galveston, Texas

## ● TABLES OF PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

*H. Gysel.* Verlag Birkhauser, Basel, Switzerland, 1951. xxii + 637 pp. 17 × 24.5 cm. 125 fr.

This volume contains the percentage atomic compositions and molecular weights of formulas containing C,H,O and N for $C_1$ to $C_{122}$. These tables will be useful, as a desk reference, to those chemists having a frequently recurring need for such information. However, since this information can be obtained rapidly in each case by use of a calculator, either mechanical or slide rule, the occasional user will find little purpose in purchasing this volume.

F. T. WEISS

Shell Development Company
Emeryville, California

INTERSCIENCE

## STATISTICAL METHODS FOR CHEMICAL EXPERIMENTATION

**(Interscience Manual #1)**

By **W. L. Gore,** *E. I. du Pont de Nemours & Company, Wilmington, Delaware.*

This manual describes how the present knowledge on design of experiments can be applied in chemical investigations. It contains a collection of methods frequently employed by the author in connection with his work in one of the largest industrial research organizations in the world.

*1952. 4 7/8 x 7. 224 pages, 20 illus., 47 tables. $3.50*

## INK AND PAPER IN THE PRINTING PROCESS

By **Andries Voet,** *Director of Ink Research, J. M. Huber Corporation, Borger, Texas.*

This book represents graphic arts research in the true sense by making apparent the correlations between raw material and finished product. It is written both from the laboratory point of view and from the practical experience of the author over a period of many years in research and in industry.

*1952. 6 x 9. 220 pages, 79 illus., 19 tables. $5.90*

## THE YEASTS: A Taxonomic Study

By **J. Lodder,** *Netherlands Yeast Factories,* and **N. W. J. Kreger-Van Rij,** *Yeast Division, Central Mold Bureau, Laboratory for Microbiology, Delft, Holland.*

The primary purpose of this book is to serve as a manual for the identification of the yeasts. But it aims at being more. The species are not only classified but fully discussed; synonyms and the original description are given, the characteristics of each species are then formulated in a standard description, and details on the origin of the culture are added. Concluding the discussion of each genus are extensive references to the literature.

*1952. 6 x 9. 670 pages, 270 illus. $19.80*

## MOLECULAR THEORY OF FLUIDS

By **H. S. Green,** *Institute of Mathematical Physics, University of Adelaide, S. Australia.*

This is an account of the general properties of fluids, in terms of molecular structure. A rigorous quantitative treatment of the subject is rendered intelligible to the reader with a modest mathematical equipment. Along with the mathematical development, this book presents a qualitative or semiquantitative description in purely physical terms.

*1952. 6 x 9. 280 pages, 12 illus. $5.75*

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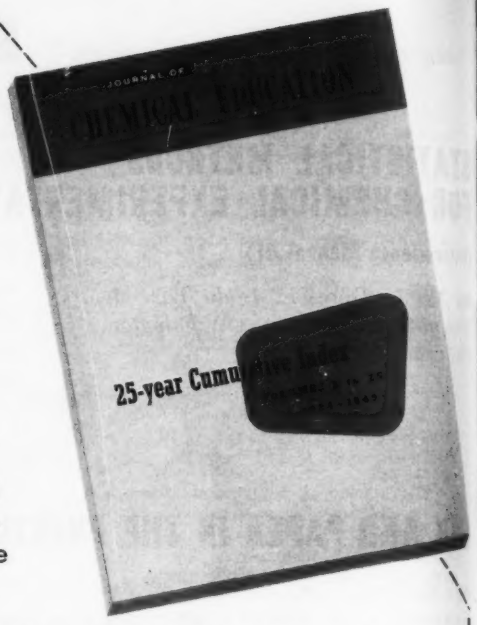


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## Spectrophotometric solvents

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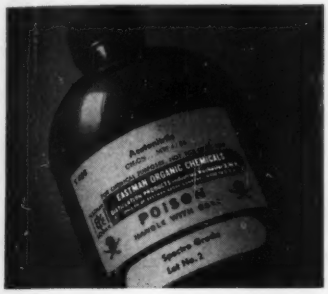


chloroform, cyclohexane, carbon tetrachloride, methanol, iso-propyl alcohol, etc., but highly uncommon is the freedom required from optically absorbing impurities. The primary producers from whom these solvents flow by the tank car are rarely prepared to supply them in spectrophotometric grade and in contamination-resistant 500 cc packaging. We are. (In special 3-liter bottles, too.) In the new 38th edition of the famous Eastman Organic Chemicals catalog we designate them by the prefix "S" before the catalog number. There are an even dozen of them (so far), and we shall be happy to send you a small wall chart that gives their infrared "windows" and ultraviolet cut-offs.

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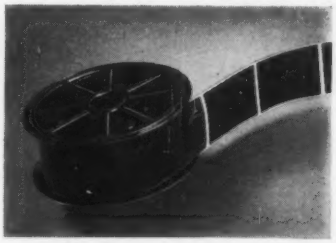

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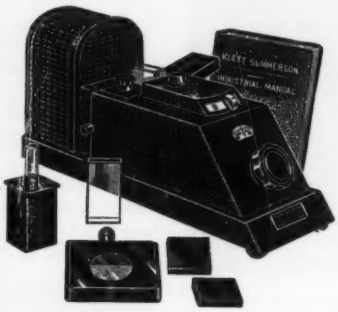

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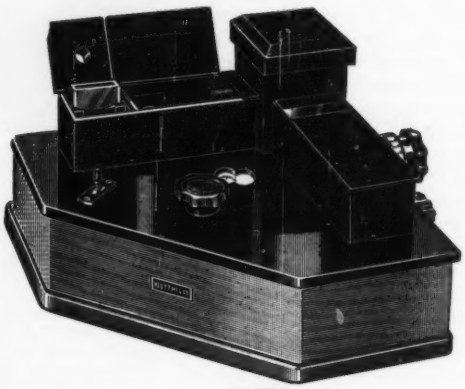

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FLAME PHOTOMETRY SPEEDS INFANT BLOOD STUDIES
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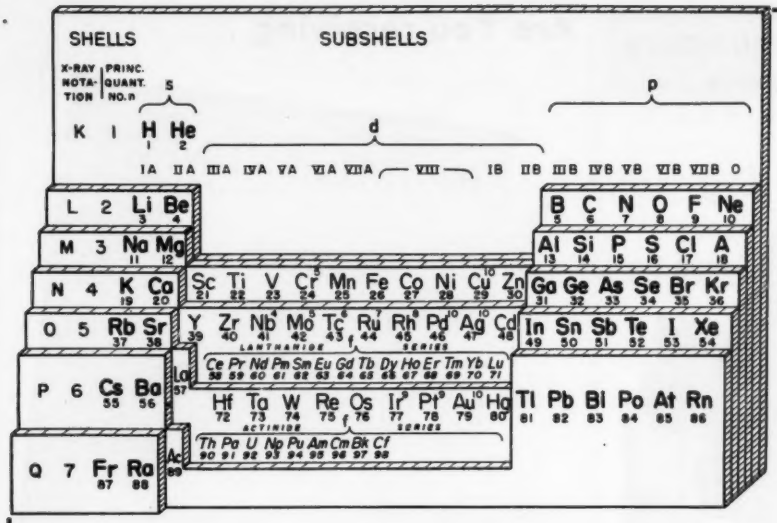


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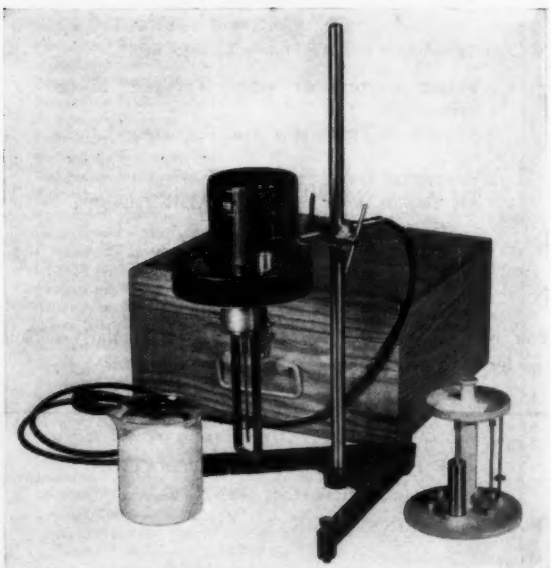

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# Out of the Editor's Basket

### First Fellowship in Chelate Chemistry

Dr. Frederick C. Bersworth, President of the Bersworth Chemical Co., has just announced the Bersworth Fellowship in Chelate Chemistry. The new Fellowship provides for one year of graduate study and research at any accredited institution of the student's choice in the U. S. or under the jurisdiction thereof. It is open to all U. S. citizens who have completed at least one year of graduate study and are currently working toward their Doctorate in any major branch of science. The stipened is $3500 payable in advance.

The Selection and Advisory Committee will announce the first award in the spring of 1953. This Committee consists of a distinguished group of internationally known chemists.

The purpose of the Bersworth Fellowship is to "encourage research on metal chelates and on the control of cations in solution in the fields of pure chemistry and in its applications to industry, agriculture and medicine."

Chelation is a comparatively new chemistry. From it have already sprung many new processes, improvements, and advances of proved benefit to all. It makes possible the stabilization of whole blood, provides remedies for heavy metal poisoning, supplies treatment for iron chlorosis in citrus trees, and permits decontamination of radioactive deposits—to say nothing to dozens of amazing applications in industry.

Application for the new Fellowship should be made directly to Dr. Arthur E. Martell at Clark University in Worcester, Mass. A Standard Application Form and a copy of the Fellowship Terms will be provided on request. The Bersworth Chemical Co. manufactures Chelating Agents known as the "Versenes." Based on the first few years of experience, it is Dr. Bersworth's intention to make the Bersworth Fellowship a continuing one with a view to an expanding Fellowship program.

### New Barnstead Central Supply Still

To meet the growing trend of including a Central Supply in new hospital construction and renovation the Barnstead Still & Sterilizer Company of Boston has engineered its new compact, space-saving Central Supply Still. Although thus far marketed mainly for hospitals, where it has gained immediate acceptance, this model also is proving its value in educational and industrial laboratories.

The famous Barnstead Type "Q," pyrogen-removing water still has been combined with a handy 12 gallon Pyrex tank in a compact wall mounting arrangement. The water still has a capacity of 10 gallons of high purity distilled water per hour. Unions used in mounting the unit can be easily loosened, making for speedy installation. Designed for the smallest wall space possible, the new Barnstead Central Supply Still is now in full production and complete information and literature may be had by writing to Barnstead Still & Sterilizer Co., 108 Lanesville Terrace, Forest Hills, Boston 31, Mass.

### Northam Frequency Computer

The Northam Frequency Computer is the result of a development for the Navy to provide a simple and accurate frequency measuring unit for a flow-metering system. This system is used for the continuous measurement of flow of difficult fluids. The primary element generates electrical pulses with a frequency proportional to the flow rate.

The Computer is operable with pulses as low as 1 millivolt in amplitude. Ranges of 5–100 cycles per second and higher with an accuracy of ±0.5% full scale are available.

The Northam Frequency Computer can be made to measure directly the frequency of any source in the audio range; measurement of higher frequencies can be accomplished by using dividers. In addition to the flow meter application, this Computer


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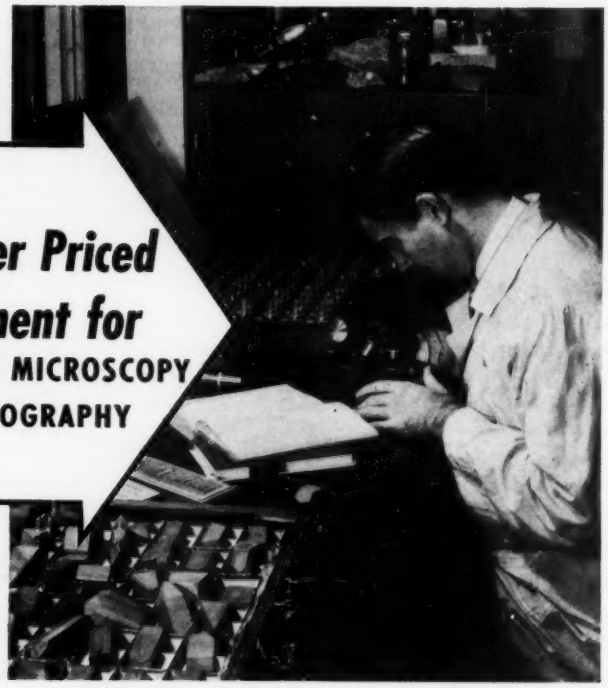

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**Scientific Manpower**

A statement recently issued by the Engineering Manpower Commission of Engineers Joint Council, reads in part:

"With the balance of manpower supply in favor of our potential enemies, it is of the utmost importance that we make the most effective use of what we have. This utilization is not merely a problem of furnishing men in uniform for military service. It also involves a coordinated plan for strengthening productive agencies—designing and developing equipment to continually improve our standards of living and ability to produce; designing and developing better equipment for defense.

"Any successful program of defense must take into account that the survival of the United States as a free nation will depend on *superior scientific and engineering skills* to offset the superiority in numbers of men which free nations lack. In addition to an overall deficit in numbers for our military forces, we are faced with a critical shortage of persons having specialized skills and experience, especially in the fields of engineering and science.

"A basic consideration is the necessity for training and developing the specialists we need in the future—engineers, scientists, diplomats, doctors, farmers, professional military personnel. We must not repeat the mistakes we made in World Wars I and II when training for civil pursuits was, to a major extent, suspended to meet the emergency of the period. We must realize that we now face a situation of indefinite continuance, not a brief or transient one.

"Should there be all-out war, the requirements of the Armed Forces will be great. It may be assumed that every physically fit young man is destined to serve in uniform, *unless it can be shown by clear and convincing evidence that he can serve the nation to better advantage in industry, agriculture, or some other pursuit which vitally affects the national health, safety, and interest.*

"The policy which we advocate would involve withholding from the total pool of men of military age, presently numbering 10,000,000 physically fit between the ages of 18 and 30, only those of the highest technical and professional qualifications, and reasonable numbers of trainees to attain such qualifications. The screening procedure will involve selection of the very highest order and must be conducted with great care if public confidence is to be maintained. This policy would require the deferment of about 500,000 young men, or 5% of the age group in question. This 500,000 constitutes a segment critical to present and future technical superiority. Otherwise, the re-

quirements for technical manpower must be met out of the pool of older men, women, 4F's, and under-age persons, and the flow of younger men into technical fields will be interrupted. The young engineer is in many cases equally, sometimes even more, in demand than his more experienced confrere, for much of the technology now critically important is so new that only recent students have any training whatever in its application. A belief that the technical requirements of industry can be met by men generally over military age—even if there were enough of them—is therefore a fallacy."

### Control Improved in Temperature Humidity Cabinet

A new development in control makes it possible to hold humidity within one degree wet bulb in Aire Regulator Temperature and humidity cabinets. Temperature is controlled by thermostats which turn heaters or open valves admitting a coolant. Humidity is controlled by a wet bulb device which atomizes water into a separate chamber through which the air is circulated. The new development is a method which avoids overloading the air during the lag waiting for the wet bulb thermostat to respond. During this period atomization is controlled by a relay which opens the spray valve intermittently for a few seconds at a time. The result is a flat line on the humidity chart instead of peaks and valleys.

Full information is available from Food Technology, Inc., 5903 Northwest Highway, Chicago 31, Illinois.

### Sterilizing With Cobalt-60

A study of advanced methods of sterilizing drugs by irradiation shows radioactive cobalt-60 to be superior, according to scientists at Armour Research Foundation of Illinois Institute of Technology.

Current methods of killing unwanted bacteria by irradiation—X-rays, beta rays, ultraviolet, high energy electron bombardment, and radioactive slurry—either have commercial disadvantages or don't do the job very well. Sterilization by heat, pressure, or chemical means reduces the effectiveness of many drugs, shortens their shelf life, or both. Cobalt-60 promises to combine simplicity of sterilization, higher efficiency, and less expense.

The irradiation unit proposed by the Foundation involves little more than a hole in the ground—lined with lead and sealed with a lead cap—and a thick concrete wall to protect the operator. Pieces of the radioactive material are placed within a carefully calculated pattern.

### Atometer

The Atometer is a small, easy to use, low-cost instrument for the estimation of gamma radiation in the event of an atomic disaster, suitable for use by the civilian population. It is 2 in. long, 3/4 in. in diameter, weighs 1 oz., and contains a solution which changes color when exposed to gamma radiation. The degree of exposure is determined by matching the color of the liquid against a color chart printed on the outside of the device.

Approximately 1/5 of the surviving casualties of an atomic bombing would suffer chiefly from radiation sickness. The Atometer is a source of information about a person's exposure to radiation that may prove of great value in assisting a doctor to make prompt diagnosis and prescribe appropriate treatment, and thereby reduce the number of those fatally injured. It is manufactured by Magnex Corp., 90-28 Van Wyck Expressway, Jamaica 18, New York.

### Evaporation Technique

Evaporation techniques for the adhesion of electroplatings and solders to oxide-coated metals and glass have shown great progress at the Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

Some metals are difficult to electroplate or solder due to poor adhesion to their natural hard tenacious oxide coatings. When these coatings are removed new oxides are immediately formed. Metals such as aluminum, chromium and titanium become coated with an oxide film even at room temperature in a vacuum at pressures less than $10^{-5}$ mm. Hq. Hence, it is desirable to secure adhesion to these metals by a process which includes their


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oxides. Excellent adhesion to these oxides can be obtained by high-vacuum evaporation techniques. Evaporated films of most metals that form hard adherent oxide coatings can be caused to adhere tenaciously to their own and to other oxides, including glass. Evaporated films of some other metals, particularly gold, silver, and copper show poor adhesion to oxides. However, a metal of the latter group can be made to adhere tenaciously to a metal of the former group by high-vacuum evaporation techniques. The vapors of the two metals can be deposited simultaneously in such a manner as to eliminate the oxide coating which normally hinders adhesion. Thus, to coat titanium with copper, titanium is first evaporated on the oxide-coated titanium. At the first evidence of titanium deposition the evaporation of copper is begun. At the first copper deposit the titanium source is turned off and the copper evaporation continued until no titanium shows through the surface. The resulting surface can be soldered to directly or can be built up by electroplating. This method can be adapted to coating rolls or flat plates in a continuous coater.

### Ion Exclusion

Ion exchange resins are agents in a promising new industrial process called "ion exclusion" which will simplify the removal of materials from solutions, The Dow Chemical Co., Midland, Mich., has announced.

The process separates a non-ionic substance from an ionic substance in a solution by rinsing the solution through a bed or column of ion exchange materials. An example of its operation is the separation of salt and an alcohol in a solution into their respective pure solutions. This may be done by introducing a small volume of the original mixture into the top of a column or container of ion exchange resin and rinsing with pure water. If the flow rate and column dimensions are right, the salt solution will come out ahead of the alcohol solution. It differs from ion exchange which requires a regenerating chemical to restore the resin for repeated use. In ion exclusion the rinse water used in the separation process in effect regenerates the resin for re-use.

### Lead

"Lead in Modern Industry" is the title of a new, fully illustrated, 230-page, cloth bound book that has just been published by the Lead Industries Association. This is the only book currently available whose subject matter is devoted exclusively to the manufacture, applications, and properties of lead, lead alloys, and lead compounds. It was written to provide the public in general with a broad picture of the whole lead industry and, at the same time, serve as a handy reference source for those who are already using lead and its products. It is sufficiently technical to be of practical value to the engineer in industry and yet broad enough for those with a more casual interest.

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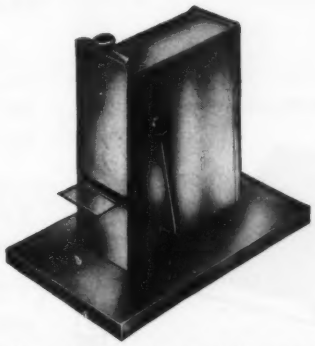

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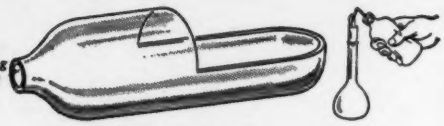

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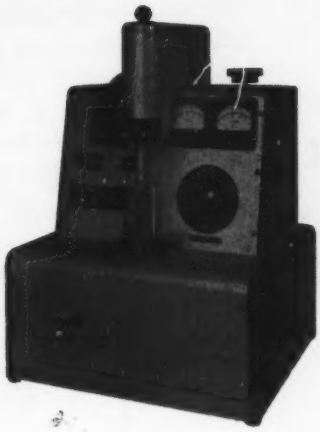

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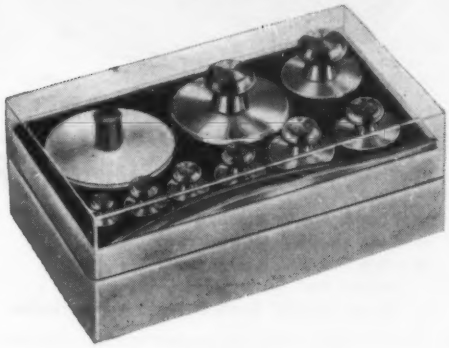

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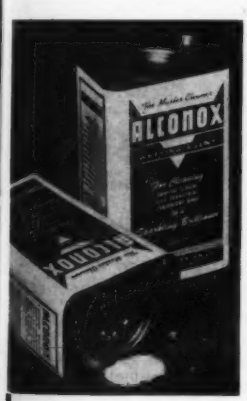


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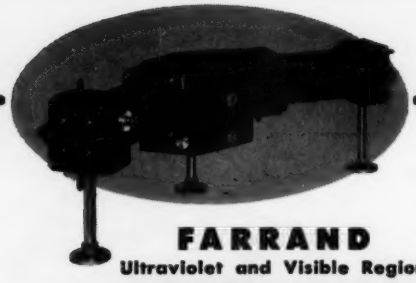

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Remsen's work as a university president and a public servant constitute another example of the vicissitudes of an honest scientist in local and national politics and they are well told. Seeing the elaborate bibliography of Remsen's publications appended to this book we have the feeling, even after the pleasant hours spent in reading it, that most has not been made of the evolution of Remsen's practical and theoretical work as seen against the background of American organic chemistry of those days. Should anyone later attempt to write this more elaborate biography he will surely find this book a handy collection of facts to start from.

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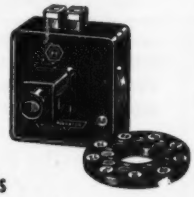

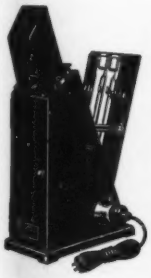

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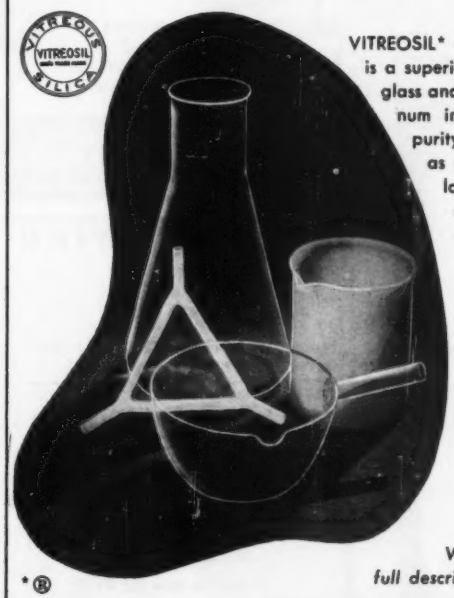


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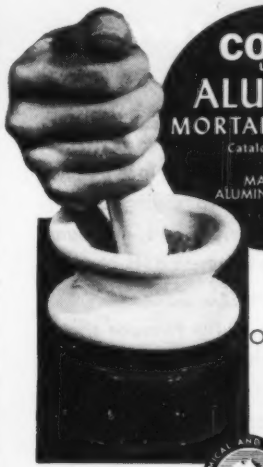

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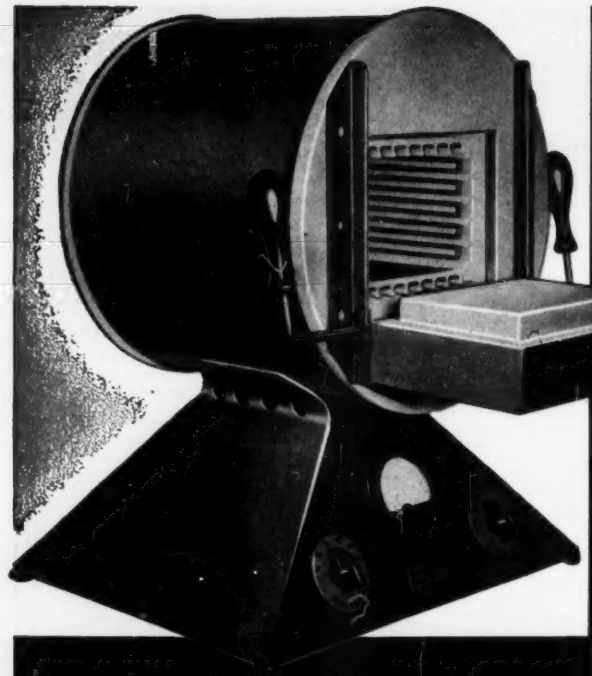

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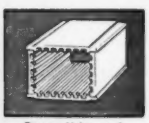

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